DEC 15 1939

THIS NUMBER COMPLETES VOLUME 48

Volume 48 December, 1939 Number 6

SOIL SCIENCE

Founded 1916 by Jacob G. Lipman

Associate Editor
HERMINIE BROEDEL KITCHEN

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Published Monthly by THE WILLIAMS & WILKINS COMPANY
MT. ROYAL AND GUILFORD AVENUES, BALTIMORE, MARYLAND, U. S. A.

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FOUNDED BY
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RUTGERS COLLEGE, NEW BRUNSWICK, N. J.

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Entered as second-class matter, May 12, 1919, at the post office at Baltimore, Maryland, under the act of March 3, 1879.
Subscription price $5.00 per volume. Single numbers, $1.00

THE INFLUENCE OF THE DEGREE OF SATURATION OF SOIL COLLOIDS ON THE NUTRIENT INTAKE BY ROOTS

H. JENNY AND A. D. AYERS

University of California[1]

Received for publication August 14, 1939

In order to elucidate mineral nutrition of plants in soils, plant physiologists have developed the method of artificial culture solutions of known compositions. For almost a century this method proved most fruitful, and it has furnished the fundamental principles of present-day knowledge of mineral nutrition of plants. With the advance of the study of colloidal phenomena in soils, especially with regard to the role of colloids in influencing the composition of the soil solution, it became apparent that the artificial nutrient solution medium was an inadequate basis for interpretation of the actual growth conditions existing in many soils. Here the simple system "root/solution" is complicated by the presence of colloidal clay particles which compete with the plant root for certain nutrient elements. Consequently, in recent years the study of absorption of nutrients by plants in the presence of colloidal suspensions of known compositions has come into prominence (1).

STATEMENT OF PROBLEM

Nutrient ions which are adsorbed on the surfaces of clay particles are a part of the diffuse electrical double layer and cannot be accumulated by plants unless first displaced from the sphere of attraction of the clay micelle. Several types of mechanisms may be operative in the process of liberation of cations adsorbed on clay particles. In the special case of K-clay, for example, release of potassium may be brought about by:

Hydrolysis. The H ions of water replace the adsorbed K ions.

Acid exchange. H ions from acids dissolved in the soil solution, particularly carbonic acid and nitric acid, exchange K ions from the surface of clay particles.

Salt exchange. Many soils of arid regions contain considerable amounts of inorganic salts ($CaCl_2$, Na_2SO_4) which participate in exchange reactions.

According to the soil solution theories of plant growth in soils, ionic exchange between soil solution and clay surfaces is a prerequisite for the intake of adsorbed ions by plants. In other words, the mechanism of nutrient absorption by roots in colloidal suspensions involves—in contrast to solutions—not

[1] Division of Plant Nutrition, College of Agriculture, Berkeley, California. The experimental data have been taken from Dr. Ayers' thesis: "The intake of potassium by excised barley roots from solutions and colloidal clay suspensions."

one step but two steps. In true solutions, as soon as an ion or ion-pair strikes the root surface, it is ready for intake, whereas in colloidal solutions this step must be preceded by the release of the ion from the surface of the clay particle. As a general rule, the plant itself provides the necessary replacing agents. It may be aided in considerable part by the action of microorganisms.

The present study deals with a comparison of the intake of potassium from colloidal clay systems and from true electrolyte solutions. Special emphasis is placed on the influence of the degree of saturation of colloids because this is one of the major factors governing the availability of adsorbed ions in soils. No effort is made to evaluate the contact exchange theory of Jenny and Overstreet (9), which provides an additional mechanism of plant nutrition in soils.

The presentation of the data embraces the following parts:

Theoretical and experimental study of ionic exchange as dependent on the degree of saturation, with special reference to the exchange with carbonic acid.

Accumulation of adsorbed K from clay suspensions by barley roots.

Accumulation of K from salt solutions which contain identical amounts and proportions of total K as the colloidal solutions.

On the basis of these comparable sets of data, it should be possible to elucidate quantitatively the differences in nutrient-supplying power of solutions and suspensions.

ION EXCHANGE AND DEGREE OF SATURATION

Simple exchange reactions of the type,

$$\left[\text{Clay}\begin{matrix}\text{K}\\\text{K}\end{matrix}\right] + 2\text{NaCl} \rightleftharpoons \left[\text{Clay}\begin{matrix}\text{Na}\\\text{Na}\end{matrix}\right] + 2\text{KCl},$$

may be expressed quantitatively by thermodynamic (15) or kinetic equations (7). In natural soils, pure clay systems (e.g., K-clay, Na-clay, etc.) are rarely found. The colloidal clay particles almost always carry a variety of cations.

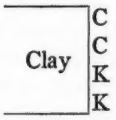
If a specific cation, say potassium, is singled out, the remaining adsorbed cations (Na, Ca, H, etc.) may be designated as *complementary* ions. The relationship between K and the complementary cations is known as *degree of saturation*, which is usually expressed on a percentage basis. The degree of K saturation is defined as

$$\frac{\text{K}}{\text{K} + C} \times 100,$$

where C denotes the amount of the exchangeable, complementary cations, and the sum $(\text{K} + C)$ corresponds to the saturation capacity of all colloidal particles present in the system.

From the viewpoint of mineral uptake by plants in soils, the degree of saturation assumes a dominant role because it controls the exchangeability, and

therefore the availability, of nutrient ions. Let us, for example, consider the following type of cation coating of a clay particle:



If we place the particle in a solution which contains a third cation, say NH_4, the amount of K replaced depends on the number of complementary cations present on the surface, in other words, on the degree of K saturation. Moreover, the kind of complementary ions also is of importance. If these ions are held loosely, they will tend to depress further the outgo of potassium. Evidently the replacement of adsorbed K in a multiple-ion system is governed by rather complicated interactions of adsorbed and released cations.

It will be instructive to isolate the role of the degree of saturation and the nature of the complementary cation for a relatively simple system. Let us assume that a colloidal particle contains exchangeable cations of the type "B" (corresponding to the special case of potassium) and complementary cations "C." To this system we add a solution containing ions of the type "W" in amounts equal to the number of "B" ions in the system (symmetry concentration). In general such systems may be prepared by mixing the following substances:

$$\text{B-clay} + \text{C-clay} + \text{W-salt}$$

A special case may be represented by the following example:

$$\text{K-clay} + \text{Na-clay} + NH_4Cl$$

The essential problem with which we are dealing is this: How many B ions will be replaced by W ions if the amount and kind of the complementary C ions vary within wide limits?

A mathematical expression which answers the foregoing questions may be derived according to reasoning previously developed (7) for an idealized ionic exchange model. The equation has the form:

$$b^2\left(2\frac{V_c}{V_b} - 2\right) + bb_0\left[\frac{V_c}{V_b}\left(\frac{1 - 2D}{D}\right) + 3\right] - b_0^2 = 0 \qquad (A)$$

The symbols have the following meaning: b_0 = number of B ions initially ad-(orbed, b = number of B ions replaced, D = degree of saturation of B ions sdivided by 100), V_b = oscillation volume of B ions (taken to be equal to V_w, the oscillation volume of W ions), V_c = oscillation volume of C ions.

It will be noted that the equation contains the two required variables D, degree of saturation, and V_c, the adsorbability of the complementary ion. Three typical, calculated curves are given in figure 1. They reveal several striking features.

First, the curves clearly show that a decreasing degree of saturation reduces

the amount of B ions replaced by W ions. For the specific case in question, the W ions will replace 50 per cent of the B ions, if no C ions are present (degree of saturation of B is 100 per cent). The replacement of B approaches zero when the proportion of C ions to B ions on the colloid becomes very large.

In the second place, the influence of the nature of the complementary ion is highly significant. Three characteristic cases are illustrated in figure 1. If the C ions are held by the particle more tightly than are the B ions, the replacing W ions favor the B ions and the degree of saturation has little effect as long as it does not fall below 25 per cent (upper curve). If, on the other

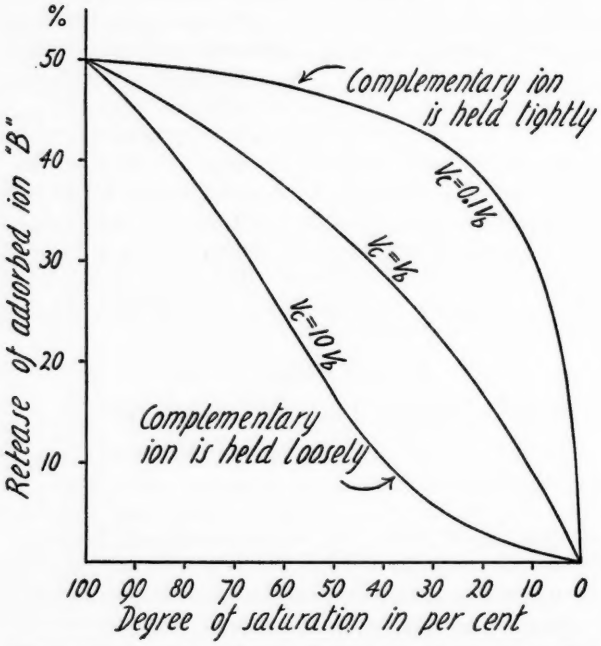


FIG. 1. THEORETICAL EXCHANGE CURVES, SHOWING THE INFLUENCE OF DEGREE OF SATURATION AND NATURE OF COMPLEMENTARY ION

hand, the complementary ion is held loosely, as compared with B, the replacing agents will exchange C rather than B and the role of the degree of saturation assumes formidable proportions (lower curve). If all ions possess equal oscillation volumes, that is, equal adsorbability, a relationship results which is indicated by the middle curve. The arbitrarily selected ratios (10:1) of the oscillation volumes are conservative. In the case of adsorbed Na and H the shape of the curves would be highly exaggerated, since $V_{Na} : V_H$ has a value of 200 [compare (7)]. Vageler (14) also has developed an equation which describes base exchange as a function of the degree of saturation. It is essentially of

empirical nature and does not stress the significance of the properties of the complementary ions.

An experimental illustration of the foregoing theoretical discussions is presented in figure 2. It refers to K-clay systems to which were added various amounts of Ca-clay, or Na-clay, or NH_4-clay. The exchanging electrolyte was HCl. The concentrations of K (as K-clay) and of HCl were 1 m.e. per liter. Although the type of ions does not quite conform to the assumptions postulated in the equation (especially $V_K \neq V_H$), the general relationships are

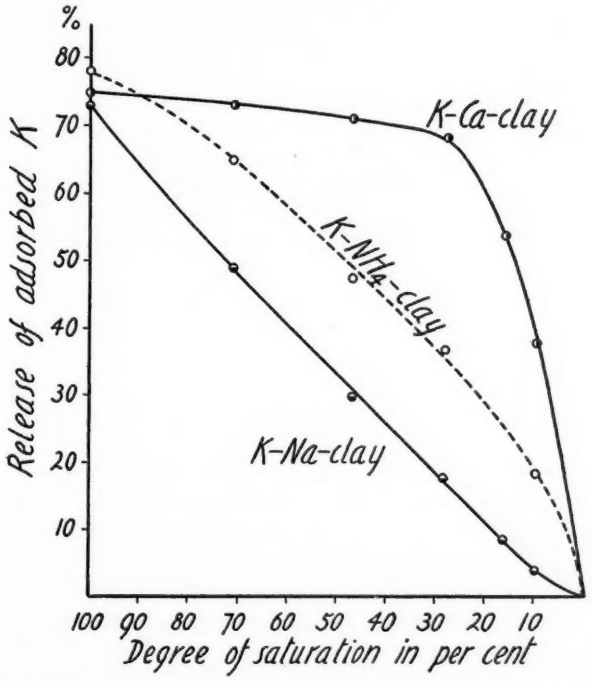


FIG. 2. EXCHANGEABILITY OF ADSORBED K AS INFLUENCED BY DEGREE OF SATURATION AND NATURE OF COMPLEMENTARY ION. EXCHANGING AGENT: HCl

nevertheless clearly indicated. The adsorbability of the complementary ions decreases from Ca to NH_4 to Na, and the shapes of the curves are correspondingly manifested.

SOME BIOLOGICAL CONSIDERATIONS

Although theory and experiment demonstrate that the release of adsorbed ions decreases with lowering of the degree of saturation, it does not necessarily follow that the intake of adsorbed potassium by roots follows the same trend, for plants possess an inherent ability for pronounced selective absorption of

solution ions. The following considerations may throw some light on the relationships to be expected.

The experiments just cited show how much K is exchanged by a given amount of H ions under a given set of conditions. One might reverse the problem and ask the question: How high an amount of electrolyte must be added to systems of various degrees of saturation in order to exchange a constant percentage of the adsorbed potassium? For ions which are equally well adsorbed ($V_b = V_e = V_w$) the following relationship is obtained between B

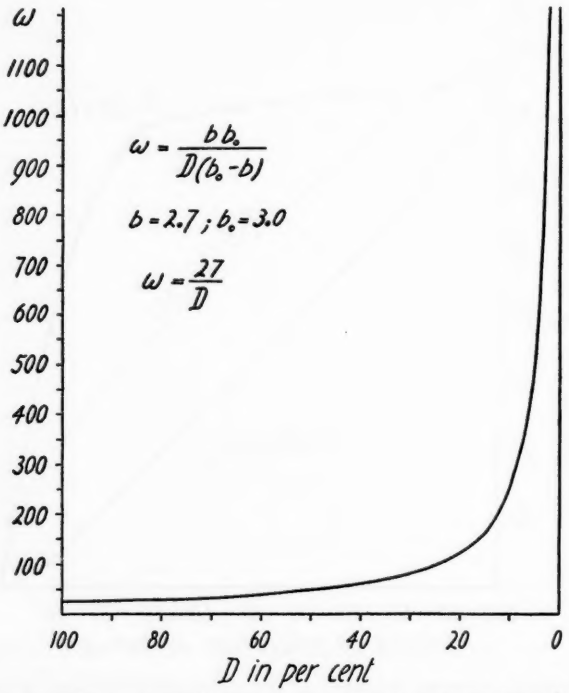


FIG. 3. AMOUNT OF ELECTROLYTE (w) NECESSARY TO REPLACE 90 PER CENT OF ADSORBED K AT VARIOUS DEGREES OF SATURATION (D)

ions initially adsorbed (b_0), B ions exchanged (b), W ions added (w), and degree of saturation (D):

$$b = \frac{b_0 w D}{b_0 + w D} \qquad (B)$$

As will be shown presently, 100 gm. of excised barley roots are able to accumulate within 10 hours about 90 per cent of the adsorbed potassium from a 100 per cent saturated K-clay containing 3 m.e. of K in 3 liters of suspension.

With the aid of the preceding equation, figure 3 has been constructed. This indicates the amount of W ions necessary to replace 90 per cent of K (B ions) at various degrees of saturation. The phenomenal rise in the concentration of W ions at low degrees of saturation is impressive. At 100 per cent of saturation 27 m.e. of W will set free the 2.7 m.e. of K mentioned above. At 1 per cent of saturation the corresponding value is 2,700 m.e. of W. Now, the aforementioned barley roots produce only 32 m.e. of carbonic acid (5) during the period of experimentation (10 hours) and this represents the maximum amount of W available for the exchange reaction. It is far short of the amount necessary to replace 2.7 m.e. K at low degrees of saturation, even if we grant that H ions are somewhat better replacing agents than the W ions of equation *B*.

It should not be forgotten, however, that equation *B* neglects the selective accumulation capacity of the roots. It is an equilibrium equation, based on the assumption that nothing has been removed from the system. During the exchange reaction the roots constantly remove replaced K and shift the equilibrium in favor of K liberation. If we designate by r the fraction of exchanged K (or B ions) removed by the roots, the following equation is obtained:

$$rb^2 - b\left[b_0\left(\frac{1-r}{D}+r\right)+w\right]+b_0w=0 \qquad (C)$$

Figure 4, which is corollary to figure 3, graphically illustrates several specific solutions of equation *C*. The x-axis contains a selected range of degrees of saturation (3 to 25 per cent). On the y-axis are plotted the amounts of replacing W ions (w) which are necessary to exchange 2.7 m.e. K. The four curves relate to various values of r, that is, the fraction of exchanged K removed from the solution by the actively accumulating plant roots.

The uppermost curve refers to $r = 0$ and is merely a part of the curve of figure 3. The curve second from the top reflects the conditions when the roots remove 25 per cent of the K replaced. Compared with the status of no removal (uppermost curve), the values of w are consistently lower, especially at the lower degrees of saturation. At $D = 3.0$ per cent, only 675 m.e. W are necessary to replace 2.7 m.e. K, instead of 900 m.e. as is the case for $r = 0$. This tendency becomes the more pronounced the greater is the amount of K removed. When 75 per cent K is consumed by the roots, the corresponding value of w is only 227 m.e. If K is removed as fast as it is released from the clay particles, the equation yields a value of 2.7 m.e. w, which represents the minimum amount of any electrolyte necessary for replacing 2.7 m.e. K. Contact exchange (9) is the only mechanism which provides so efficient a removal of ions.

Evidently, the 32 m.e. CO_2 produced by the roots may or may not be sufficient to replace 2.7 m.e. K at lower degrees of saturation. It all depends on how efficiently the plants remove the exchanged K, a point emphasized by Hoagland (4) and by Truog (12). If the rate of intake is very high and if

this is an inherent property of the plant, then the degree of saturation would have no effect on the K absorption of the roots. On the other hand, if the accumulation rate is conditioned by the K concentration and the cation ratios of the solution, the degree of saturation should play a role in the nutrition of the plant. At low degrees of saturation, the bulk of carbonic acid functioning in exchange will be consumed in the release of complementary ions (C) rather than K ions, and the K concentration in the intermicellar liquid may become

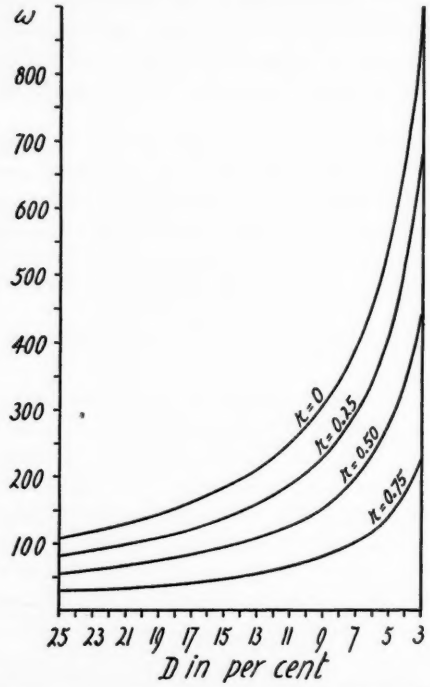


FIG. 4. EFFECT OF REMOVAL OF EXCHANGE K BY ROOTS (r) ON THE AMOUNT OF ELECTROLYTE (w) NECESSARY TO REPLACE 2.7 M.E. K AT VARIOUS DEGREES OF SATURATION (D)

so low and the C : K ratio so high as to overbalance the selective absorption tendencies of the roots.

EXPERIMENTAL TECHNIC

Clay particles having an effective settling diameter of less than 0.2 μ were separated from Yolo clay loam with the aid of Sharples supercentrifuge. Pure basic clays were prepared by leaching the colloids with salt solutions or by electrodialysis with subsequent addition of hydroxides. The base-exchange capacity of the clays varied from 59 to 67 m.e. per 100 gm. dry material.

All experiments were conducted with excised barley roots which were grown

and treated according to the method of Hoagland and Broyer (5). The roots had a high accumulation capacity for K. Approximately 100 gm. of fresh roots (about 8 gm. oven-dry) were immersed in 3 liters of the desired solutions and suspensions, which were continuously aerated. Accumulation of K was measured by analysis of the roots (3).

Special studies were undertaken to ascertain the influence of the K concentration and the time period on the accumulation of K by the roots. Both for K-clay and KCl an absorption maximum was reached at a total K concentra-

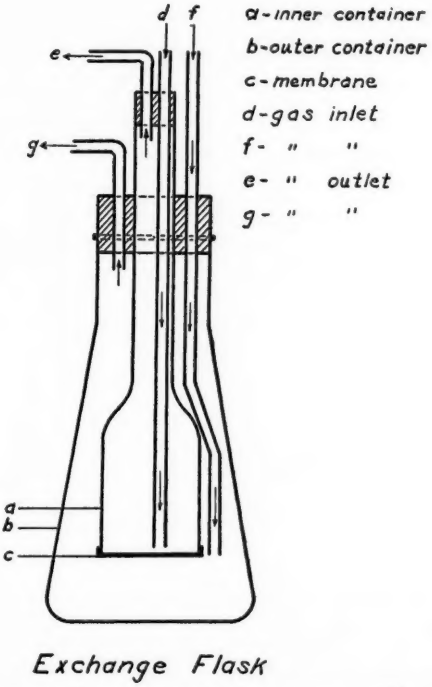


FIG. 5. EXCHANGE FLASK FOR THE DETERMINATION OF CO_2 EXCHANGE

tion of about 10 m.e. in 3 liters (10-hour periods). In all cases the roots accumulated more K from KCl than from K-clay. The time function was determined with systems containing 15 m.e. K in 3 liters. A maximum of intake was observed after 16 hours. Again the KCl solution proved to be the superior medium for K accumulation. In accordance with these findings the K level of all media was kept at about 1 m.e. total K per liter. The absorption time was restricted to 10 hours.

For the study of replacement of K from the clay suspensions by carbonic acid, a special "exchange flask" (fig. 5) was constructed which consisted of two

compartments, separated by a cellophane membrane. Clay suspension was placed in the inner container, distilled water in the outer. Carbonic acid was bubbled continuously through both compartments for 10 days. The amount of potassium found in the outer compartment was considered equal to the K concentration of the intermicellar liquid of the entire system.[2]

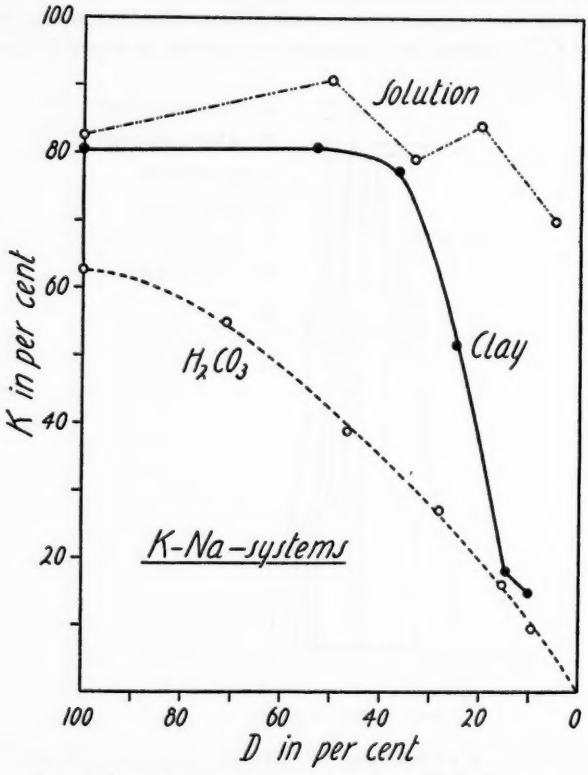


FIG. 6. ACCUMULATION OF K BY ROOTS FROM K-Na-SYSTEMS

EXPERIMENTAL RESULTS

Inasmuch as all experiments were comparable with regard to amounts and concentrations of K, type of roots, and absorption periods, it was possible to plot the results of corresponding series on one single graph. Each of the figures contains three curves, two of which express the K intake by roots from clay suspensions and salt solutions, and the third indicates the replacement by carbonic acid.

[2] The absolute amounts may be in error because of Donnan equilibria.

Potassium-sodium systems (fig. 6). From the chemical exchange curve it is evident that a saturated solution of carbonic acid replaces 62.5 per cent K from a pure K-clay (1 m.e. K per liter). With increasing amounts of Na-clay present in the system, the degree of saturation becomes lower, and the percentage of K replaced is correspondingly reduced. At very low degrees of saturation, less than 10 per cent of the total exchangeable K appears in the intermicellar liquid. The solid-line curve depicts the intake of K by excised barley roots from the K-Na-clay suspensions. Approximately 80 per cent K is taken up from the pure K-clay. The rate of change is relatively small as long as the degree of saturation does not drop below 40 per cent. As soon as the proportion of sodium to potassium on the clay becomes high, the intake of K amounts to only 15 per cent of the total K present in the suspension. No such drastic reduction is observed for the neutral salt solutions (dotted line). From pure KCl the roots accumulated 2.48 m.e., or 82.7 per cent. This value was relatively little affected by additions of NaCl, even to the extent of 57 m.e.

TABLE 1

K-Ca-systems

DEGREE OF SATURATION	CO_2 EXCHANGE	ACCUMULATION OF K FROM	
		K-Ca-clay	KCl + $CaCl_2$
per cent	*per cent*	*per cent*	*per cent*
100.0	56.6	80.5	82.6
30.0	55.5	....	....
25.0	52.5	89.5	....
20.0	48.0	....	77.6
14.6	40.0	68.2	....
10.5	31.0	50.0	....
10.0	30.0	....	101.1
5.0	16.0	....	91.5

in 3 liters solution. The initial pH values varied from 7.35 to 7.50 for the clays and from 5.60 to 5.70 for the salt solutions. At the end of the experiments the pH of the suspensions dropped to the range of 4.60 to 6.04; the solutions had values from 4.70 to 4.80.

Comparison of the three curves conclusively shows that the lack of K accumulation at low degrees of saturation is a consequence of the ion-exchange principles involved in the liberation of the adsorbed K.

Potassium-calcium systems (table 1). Substituting Ca in place of Na yields a new series of exchange and accumulation curves. First, the replacement of K by H_2CO_3 is scarcely affected by the presence of Ca as long as the degree of K saturation remains above 30 per cent. Unlike Na, Ca is held very tightly on the surface of the clay particles, and consequently, the H ions of carbonic acid readily exchange K ions. The same trend is observed for the accumulation curve. Although the analytical data scatter considerably, the total uptake of K remains relatively high at all degrees of saturation investigated.

At 10 per cent potassium saturation, the roots still obtained 50 per cent of all K present, whereas for the K-Na-clay the corresponding value was only 14.8 per cent. The K accumulation from chloride solutions appeared to be stimulated by the addition of $CaCl_2$. This again points to the fact that any retardation in absorption of K by roots is related to the exchangeability of K on the clay particles. The initial reaction was 6.90 to 7.00 for the clays and

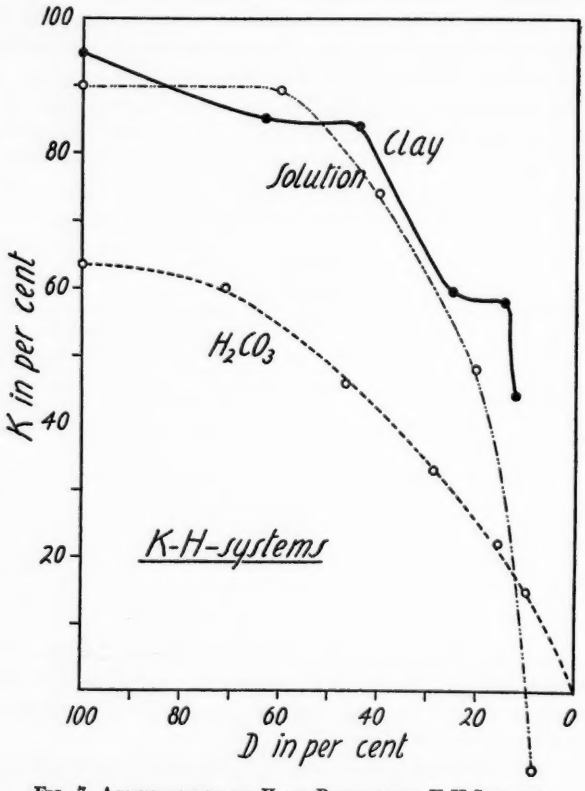


FIG. 7. ACCUMULATION OF K BY ROOTS FROM K-H-SYSTEMS

5.65 to 5.80 for the chloride solutions. The final pH values were 4.45 to 6.20 for the clays and 5.40 to 6.50 for the solutions.

Potassium-hydrogen systems (fig. 7). The presence of H ions on the clay particle brings about a gradual lowering of the exchange of K by carbonic acid. The K accumulation curve for the roots falls off in like manner. The same is true for the intake from solutions consisting of mixtures of KCl and HCl. Hydrochloric acid was injurious to the roots, as evidenced by their loss in turgor and of K ions.

It should be pointed out emphatically that the above KCl-HCl solution series gives a distorted picture of the influence of acid clays on K absorption. The pH values of the mixtures having high ratios of HCl to KCl were less than 2, whereas the corresponding clay systems were so strongly buffered that the final pH values of all suspensions fluctuated only from 4.20 to 4.35 irrespective of the degree of saturation. Hoagland and Broyer[3] have shown that the

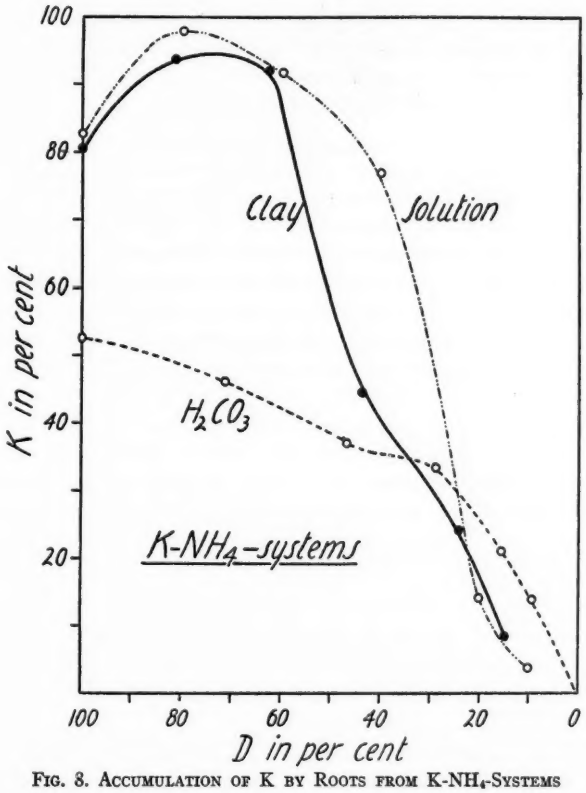


FIG. 8. ACCUMULATION OF K BY ROOTS FROM K-NH_4-SYSTEMS

intake of K by excised barley roots from solutions is relatively little affected within the pH range of 4.5–8.0. In harmony with these findings no injurious effect of the acid clays on the roots could be detected. We are thus led to the conclusion that the diminishing intake of K with lowering of the degree of saturation is conditioned by the reduced availability of potassium rather than by an injurious effect of hydrogen ions.

Potassium-ammonium systems (fig. 8). Small amounts of NH_4 ions on the

[3] Hoagland, D. R., and Broyer, T. C. Unpublished data.

colloidal particles seem to stimulate the intake of K by the roots, but as soon as the degree of saturation falls below 60 per cent, the absorption of K reaches a very low level. At 14 per cent saturation, the roots recover only 8.4 per cent of K as compared with 18 per cent for K-Na-clay, 58 per cent for K-H-clay, or 68 per cent for K-Ca-clay. This sharp decline of K consumption from K-NH_4-clay, however, is not only a consequence of exchangeability but is also conditioned by physiological processes of the roots, since in the mixtures of KCl and NH_4Cl the roots behave in a very similar manner. In place of K the roots gained considerable amounts of nitrogen, which might have impaired the absorptive capacity for potassium. The pH values were of the same order of magnitude as those of the other salt systems.

DISCUSSION[4]

Probably one of the first investigators to study the effect of the degree of saturation on plant growth was Stohmann (10). He treated acid peat with extracts of barnyard manure and then leached the material for 3 weeks with large amounts of water. In this manner he obtained peat which had virtually all of the nutrient ions in the adsorbed state. This basic peat was mixed with various amounts of acid peat and planted to corn. The weight of the mature plants, in grams, was as follows:

Growth Medium	*Yield*
100 per cent degree of saturation	836
50 per cent degree of saturation	386
25 per cent degree of saturation	252
Acid peat alone	17.5

About 10 years ago, Gehring (2) showed for a series of German soils that the degree of saturation of K in soils tends to be related to the Neubauer test and to field response for K fertilization. The lower the degree of K saturation, the greater was the yield increase brought about by application of potash fertilizers. Soils which vary widely in total amount of exchangeable K, or soils which possess a high fixing power for K, however, would not be expected to follow this simple relationship.

With the development of colloid chemical methods and theories, it was possible to approach the subject under more rigidly controlled conditions. Jenny and Cowan (8) found that the yields of soybean plants grown in Ca-H-clay suspensions sharply decreased when the degree of saturation fell below 30 per cent. Albrecht and his students (1) extended these studies to other types of cations and to microscopic organisms. In particular, Horner (6) pointed out the significance of the nature of the complementary cation.

[4] Note during publication. The translation from the Russian of an important paper by S. S. Yarussov "On the availability of soil exchangeable cations for plants," in *Pedology* 1938: 799–828, was received too late for inclusion in the discussion. Yarussov's and our viewpoints agree in essential parts.

Tyner (13), using Prianischnikov's isolation method, observed a depressing effect of half saturated K-bentonites on the growth of various plant species.

There appears to be general agreement regarding the factual data on the relationship between plant growth and degree of saturation, but as to explanations, the opinions are divided. The present study convincingly shows, both by experiment and by theory, that the replaceability of a cation from a clay particle is depressed by the presence of complementary ions. This impedance in release of ions is reflected in the accumulation by plant roots. In some cases, as with K-Na-clays, the exchange principle appears to be the sole factor which limits the amount of uptake of K by excised barley roots; in others, especially for K-NH_4-clays, some antagonistic or competitive effect of the complementary ion on the physiological absorption is strongly indicated.

According to the contact depletion theory of Jenny and Overstreet (9), plants might cease to accumulate ions at very low degrees of saturation and actually give off ions to the clay particles. This *critical degree of K saturation* was not reached in the present study, indicating that for the systems under consideration it must lie below 10 per cent potassium. Tiulin (11), who studied the availability of adsorbed phosphates, also has postulated a critical degree or zone of saturation. According to Tiulin, it is that degree of saturation below which the adsorbed ions remain unavailable to the plant. It should be pointed out, however, that on the basis of the soil solution theories, nutrients are available at all degrees of saturation, although, of course, to a lesser extent as D becomes smaller (fig. 1). The critical degree of saturation is most sharply defined by the contact exchange theory, according to which the roots accumulate elements above the critical degree of saturation and loose them below it. We believe that the critical degree of saturation is not a fixed property of the soil but depends on the type of plant and its physiological conditions.

From the viewpoint of agricultural practice, it is of interest to note that Ca is the least retarding cation in the process of liberation of potassium, a fact which again demonstrates the superiority of neutral, calcium-saturated soils. As a matter of fact, neutralizing an acid soil with Ca should render K more available, as indicated by a comparison of the K-H-curve and the K-Ca-curve. New light is shed on the problem of soil acidity. As soils gain hydrogen ions the remaining nutrient ions not only are reduced in numbers but become less exchangeable; in other words, less available for consumption by plants. Plant production suffers correspondingly. These relationships very likely play a more important part in the problem of soil acidity than the direct toxic effects of hydrogen ions in soils, for which no convincing direct physiological influence has as yet been demonstrated. It is probable that similar relationships exist in many alkali soils (Na-soils) in which Na ions constitute the bulk of the complementary cations. For equal applications of potassium fertilizer, crops should utilize a higher percentage from light-textured than from heavy-textured soils. The high exchange capacity of heavy soils brings about a low degree of saturation of potassium. The reverse is true for light

soils: the exchange capacity is low, and equal numbers of K ions make up a high percentage of the exchangeable ions. The practical consequences of these inverse relationships have been discussed in great detail by Vageler (14).

Although we have placed emphasis on the degree of saturation, we are, of course, fully aware of the importance of the magnitude of the absolute amount of exchangeable K in the soil for plant production. This is the value usually determined by extraction methods with the aid of neutral salts or dilute acids (e.g., quick tests). It appears in the equation as b_0. Our studies demonstrate, however, that the physiological availability of the absolute K level depends on its degree of saturation and the nature of the complementary cations.

SUMMARY

A quantitative theory has been developed which relates base exchange to the degree of saturation. The exchangeability of adsorbed K decreases with decreasing degree of saturation. The nature of the complementary ions markedly affects these relationships.

The physiological availability of adsorbed potassium was investigated with the aid of excised barley roots. Corresponding studies were made with true solutions containing potassium ions. In this manner, it was possible to separate K intake into the colloid chemical exchange phase and the biological accumulation phase.

Lowering the degree of saturation of K resulted in a reduced intake of the element. In accordance with the exchange theory, the rate of decline was greatly affected by the nature of the complementary cation. Calcium was least effective; ammonium had the greatest influence; and hydrogen and sodium occupied intermediate positions.

Certain practical applications are discussed.

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THE EFFECT OF NATURAL GAS ON THE GROWTH OF MICRO-ORGANISMS AND THE ACCUMULATION OF NITROGEN AND ORGANIC MATTER IN THE SOIL

HORACE J. HARPER

Oklahoma Agricultural Experiment Station

Received for publication August 11, 1939

When natural gas diffuses slowly into moist soil and the temperature is not extremely low, a white or light-colored residue soon appears on the surface of macroscopic openings occurring in the exposed area. During dry or cool weather, the color of this residue gradually changes to dark brown or black. This effect was observed by Schollenberger (5), who found, on examining a soil through which natural gas had escaped from a leak in a pipe line, that the soil exposed to the gas was dark brown and emitted an acrid odor similar to that of mud beneath stagnant water. A chemical analysis indicated that the affected soil was higher in replaceable ammonia and exchangeable manganese than was soil from an adjacent area which had not been exposed to the gas. A qualitative test of soil taken from the affected area and maintained for 6 weeks in a partially enclosed container at a favorable moisture content, indicated the presence of an abundance of nitrates. Wheat made a better growth in pots filled with soil which had been exposed to the gas than in pots containing normal soil.

Eight samples of natural gas from Oklahoma were analyzed by Burrell and Oberfell (2). Methane was the most abundant hydrocarbon present, ethane occurred in some samples, and small quantities of propane and butane were also present. No hydrogen, carbon monoxide, hydrocarbons of the olefin series, or hydrogen sulfide was found by quantitative tests. Tausz and Donath (6) have isolated soil organisms which oxidize paraffin hydrocarbons; consequently these microorganisms might be expected to develop in soils where natural gas was present in sufficient quantities to provide a source of energy and where other conditions were favorable for growth. Giglioli and Masoni (3) conducted experiments on the absorption of methane in the presence of oxygen by the methane bacteria of Kaserer and Söhngen. They found that these organisms were more numerous in the deeper parts of the soil and that the optimum temperature for growth was 30°C. They suggested that the absorption and partial transformation of methane into fixed organic material is constantly adding to the fertility of the soil.

Other investigators, according to McBeth and Scales (4), found that methane is produced directly or indirectly from the decomposition of manure and the fermentation of cellulose. In their investigations, methane was formed only

under anaerobic conditions and in highly nitrogenous media by cellulose-decomposing organisms. Methane was produced in the absence of nitrates by a methane bacillus. More recent studies have been made by Barker (1) and others on methane production and utilization by microorganisms.

EXPERIMENTAL

When natural gas escapes into a soil in sufficient quantities, grass, trees, or shrubs growing on that area are killed. In the fall of 1927, a gas line was laid at a depth of 20 inches in a park in Stillwater, Oklahoma, and a leak occurred as a result of an imperfect connection. Bermuda grass planted in the spring of 1928 failed to grow on an area about 2 feet in diameter above the leak in the pipe line. After the leak was repaired, the grass made a luxuriant growth on this area in 1929, and the grass was darker green than that on adjacent soil which had not been exposed to the natural gas. A second observation was made along the south side of a small wheat field in the southwest corner of the campus of the Oklahoma A. and M. College. A gas line was laid along the

TABLE 1

Effect of leaking natural gas on the nitrogen content of soil collected near the horticultural shed on the campus of the Oklahoma A. and M. College

SOIL NUMBER	DESCRIPTION	TOTAL NITROGEN
		per cent
1	Undisturbed soil at pipe level	.070
2	Surface soil 0″–8″ deep	.115
3	Soil in ditch above gas leak	.121
4	Soil collected around pipe and exposed to gas	.142
5	Very dark soil near gas leak	.467

edge of this field in 1926, and gas escaped in numerous places around the couplings. The land was plowed about 4 years after the line was installed, and very dark masses of soil were observed where gas leaks had occurred. Wheat planted on the soil was killed, or growth was stunted in these areas. A sample of soil collected from one location where gas had escaped was analyzed for total nitrogen and was found to contain 0.22 per cent of this element as compared with 0.16 per cent in the soil which was not affected by the gas. Other soil samples collected in the vicinity of a gas leak near the horticultural shed on the campus of the Oklahoma A. and M. College were analyzed for total nitrogen. The results, shown in table 1, also indicate that the nitrogen content of soil is increased by exposure to small quantities of natural gas escaping from a pipe line.

In order to determine whether this accumulation of nitrogen might be due to ammonia occurring in the natural gas, duplicate analyses were made by measuring 105 cubic feet of gas with a standard gas meter and passing it

through a gas-absorption tower containing dilute sulfuric acid to absorb any ammonia which might be present. The ammonia was determined by distillation and absorption in standard acid and was rechecked in a second distillation with Nessler's reagent. Less than 0.01 p.p.m. of ammonia was present in the samples. Other analyses which have been made on natural gas do not indicate that ammonia is present; consequently, it is quite improbable that an increase in the nitrogen content of a soil could be due to the absorption of ammonia from the natural gas escaping slowly into it from a leaking pipe line.

When a close examination is made of soils exposed to small quantities of natural gas, colonies of microorganisms can be seen in various stages of development, depending upon temperature and moisture conditions. White masses of slime molds are usually abundant, and myxomycetes are frequently present. A sample of soil taken about 18 inches below the surface of an area near Stillwater, Oklahoma, where gas had slowly escaped from a pipe line for several years was examined by Elizabeth McCoy.[1] She found that *Clostridium butyricus* was abundant and that other species of *Clostridium* were also present. Since these organisms are capable of fixing atmospheric nitrogen, it is logical to expect that hydrocarbons in the natural gas would supply the necessary energy either directly or indirectly for the growth and development of these microorganisms, and as a result the nitrogen content of the soil would be increased. Another sample of "gassed" soil was sent to Frances E. Clark,[2] and the following report was obtained:

> Several species of obligate anaerobes were found in dilutions up to one in ten thousand. *Clostridium sporogenes*, *Clostridium bifermentans*, and a round terminal-spored *Clostridium* were most readily recovered; the final identification of further species has been delayed by the presence of a large number of facultative anaerobes. Certain facultative species have been found in numbers of from 100,000 to 500,000 per gram. *Aerobacillus polymyxa* and *Aerobacillus macerans*, as well as *Bacillus brevis*, *Bacillus circulans*, and *Bacillus amylolyticus*, have been identified. The common aerobic *Bacilli* found predominantly in certain field soils recently studied were far from predominant in the soil submitted, for which the combined number of *Bacillus mycoides*, *Bacillus cereus*, and *Bacillus megatherium* was less than 100,000 per gram. Thus, although no control sample from adjacent normal soil was available for the spore-formers there appears to be a shift from the aerobic toward the facultatively anaerobic species.

After it appeared that nitrogen fixation was occurring in soils exposed to natural gas from leaking pipe lines, additional samples of soil were collected from several locations near Stillwater, Oklahoma, where gas had escaped or was escaping, and samples of normal soil taken from the same locality were analyzed for total nitrogen and organic matter. The results of these analyses are given in table 2.

In every soil which had been exposed to a slow infiltration of gas for a considerable length of time, the nitrogen content was increased. In some in-

[1] Department of bacteriology, University of Wisconsin.

[2] Division of Soil Microbiology, Bureau of Plant Industry, U. S. Department of Agriculture.

stances, the total nitrogen in very poor soils affected by gas was much higher than that occurring normally in some of the best soils in Oklahoma.

The average nitrogen and organic matter contents of the soils affected by gas were nearly three times as great as those of normal soils. The organic matter-nitrogen ratios of these soils were variable. The lowest ratio occurred in a "gassed" soil, and seven of the ten samples collected near gas leaks had lower ratios than the corresponding samples of soil not exposed to the natural gas. A narrow ratio would be expected from residues accumulating from micro-

TABLE 2

Effect of natural gas and growth of anaerobic organisms on the nitrogen and organic matter content of soils near Stillwater, Oklahoma

SOIL NUMBER	LOCATION	TOTAL NITROGEN		ORGANIC MATTER		ORGANIC MATTER-NITROGEN RATIO	
		Normal soil	Gassed soil	Normal soil	Gassed soil	Normal soil	Gassed soil
		per cent	*per cent*	*per cent*	*per cent*		
1	Oklahoma A. & M. College Campus South of Home Economics Building	.073	.195	2.18	4.95	29.9	25.4
2	Oklahoma A. & M. College Campus East of Horticultural Shed	.042	.085	0.77	1.44	18.3	16.9
3	Oklahoma A. & M. College Campus NW of Agri. Engineering Building	.042	.398	0.77	3.61	18.3	9.1
4	1 mi. N.; 1 mi. W. of Stillwater, Oklahoma	.164	.218	2.78	5.00	17.0	22.9
5	3½ mi. E.; 2 mi. S. of Stillwater, Oklahoma	.057	.270	1.21	3.04	21.2	11.3
6	4¾ mi. E.; 2 mi. S. of Stillwater, Oklahoma	.061	.264	1.34	3.44	22.0	13.0
7	6½ mi. E.; 2 mi. S. of Stillwater, Oklahoma	.304	.425	3.24	11.65	10.7	27.4
8	7 mi. E.; 2 mi. S. of Stillwater, Oklahoma	.076	.284	0.88	2.99	11.6	10.5
9	8½ mi. E.; 2 mi. S. of Stillwater, Oklahoma	.115	.130	1.24	2.27	10.8	17.5
10	8½ mi. E.; 2⅝ mi. S. of Stillwater, Oklahoma	.042	.398	0.77	3.61	18.3	9.1
Average		.098	.267	1.52	4.20	17.8	16.3

organisms unless some free carbon might accumulate. The very narrow ratio of the unaffected soils needs further study to determine what factors may be responsible for this condition.

An experiment to determine the availability of the nitrogen accumulating in these "gassed" soils was conducted in the greenhouse. Soils collected near the gas leaks and similar soil which had not been affected by the escaping gas were placed in gallon cans, and oats were planted in them. The oat leaves were darker and more forage was produced by the plants in the "gassed"

soil as compared with plants in the normal soil. Data on yield were lost through failure of the thermostatic control on the drying oven.

Additional soil samples collected in or near Oklahoma City, Oklahoma, to obtain further information on the effects of escaping natural gas on the nitrogen and organic matter in soil were analyzed for these constituents. The results are given in table 3. The average nitrogen content of the soils exposed to natural gas was about two and one-half times as great as that of soil taken from an adjacent area which had not been affected, and the organic matter content of the "gassed" soils was nearly three times as high as that of the normal soils.

The organic matter-nitrogen ratios of these soils, like those of the Stillwater soils, were variable. No explanation can be given for the very high ratio in

TABLE 3

Organic matter and nitrogen content of soil samples collected from normal soil and from areas exposed to natural gas from leaking pipe lines in or near Oklahoma City, Oklahoma

SOIL NUMBER	LOCATION	TOTAL NITROGEN		ORGANIC MATTER		ORGANIC MATTER-NITROGEN RATIO	
		Normal soil	Gassed soil	Normal soil	Gassed soil	Normal soil	Gassed soil
		per cent	*per cent*	*per cent*	*per cent*		
1	West Reno Street	.126	.297	2.75	10.60	21.8	35.7
2	20 ft. south of No. 1	.126	.291	2.75	10.40	21.8	35.7
3	SW¼ Sec. 36, T 12 N, R 4 W	.102	.197	2.47	7.30	24.2	37.1
4	Portland Ave. and Frisco R. R.	.060	.357	1.95	7.96	32.5	22.3
5	Portland Ave. and 23th Street	.044	.129	1.60	4.60	36.4	35.7
6	Portland Ave. and 56th Street	.112	.258	2.67	8.25	23.8	32.0
7	Portland Ave. and 63rd Street	.028	.157	1.10	5.60	39.3	35.7
8	E½ Sec. 22 T 10 N, R 4 W	.073	.260	2.60	3.37	35.6	13.0
9	400 ft. south of No. 8	.151	.157	5.40	5.60	35.8	35.7
10	63rd St. and Santa Fe	.044	.134	1.40	4.80	31.8	35.8
11	1 mi. N. of Cushing, Oklahoma	.036	.092	1.24	4.71	34.4	51.2
12	1 mi. N. of Cushing, Oklahoma	.101	.106	2.75	3.70	27.2	34.9
Average		.084	.203	2.39	6.41	30.4	33.7

some of the normal soils. One of the "gassed" soils had a low organic matter-nitrogen ratio, but the majority of the soils had very high ratios as compared with those of samples collected near Stillwater. Whether carbon has accumulated in these soils or whether organic compounds having a wide carbon-nitrogen ratio were produced by other microorganisms which were present was not ascertained in this study.

It is not improbable that nitrogen accumulation observed in many areas of idle land may be due to nitrogen fixation occurring as a result of the growth of microorganisms during periods when anaerobic soil conditions prevail. When natural gas was passed rapidly through soil placed in containers in the laboratory, moisture was removed and no apparent growth of microorganisms

occurred. In order to study the growth of microorganisms under controlled conditions, several samples of soil were treated with different fertilizers and placed in quart jars each containing a thin layer of white sand in the bottom. One liter of natural gas was passed into each jar every day through a glass tube which extended into the sand. After 5 weeks, the soils were examined, and slight development of microorganisms was observed. Further study is needed to determine the optimum environmental conditions for nitrogen fixation when natural gas passes slowly through soil.

SUMMARY

Observations of areas where natural gas was escaping from leaking pipe lines into the soil indicated that microorganisms were active when moisture and temperature were favorable for growth.

Dark-colored residues accumulate in soils exposed to natural gas and remain for several years after the gas leaks are repaired.

Analyses of soil samples for total nitrogen indicate that a marked increase of this element occurs in the affected areas. Species of *Clostridium*, which are capable of fixing nitrogen under anaerobic conditions, were present.

The organic matter-nitrogen ratio was not constant in samples collected from different areas. The exact cause of this condition was not determined.

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THE ADSORPTION OF PROTEINS BY MONTMORILLONITIC CLAYS[1]

L. E. ENSMINGER[2] AND J. E. GIESEKING[3]
Illinois Agricultural Experiment Station

Received for publication August 11, 1939

Soil organic matter has several characteristics which suggest that it may be combined with the clay fraction of the soil. Its resistance to oxidation in clay soils, its immobility in clay soils, and the difficulties involved in separating the organic and inorganic soil colloids in the laboratory, are observations which indicate that a combination may exist between these two fractions. The investigations of Demolon and Barbier (1), Mattson (3), Meyers (4), and Gieseking (2) show that various organic substances have a tendency to react with clays. According to Demolon and Barbier, humic colloids are strongly adsorbed by clay when the hydrogen-ion concentration of the system is high. Mattson found the isoelectric point of proteins to be lowered by the addition of bentonite. He explained this change by suggesting that bentonite forms a nonionized compound with proteins. Meyers observed that organic colloids mixed with inorganic soil colloids showed a reduction in cation exchange capacity from the sum of the capacities of the two components. He also observed that the tendency of organic colloids to combine with the inorganic soil colloids was greater in acid suspensions. He suggested polar adsorption as the probable reaction involved. Gieseking found complex organic cations to be strongly adsorbed within the variable portion of the (001) spacings of montmorillonitic clay crystals. These complex cations replaced the hydrogen from electrodialyzed montmorillonite, resulting in larger (001) spacings.

The chemical properties of the base-exchange clays and soil organic matter are of a nature that should permit combinations to exist between these fractions. The tissues of animals and plants contain most of their nitrogen in a basic form, or a form that becomes basic upon hydrolysis. Organic matter derived from these sources will be capable, therefore, of reacting like basic compounds. This should make possible a combination between the basic or positive spots of the organic matter and the acidic or negative spots on the crystal lattice of the clay. In fact, individual particles of soil organic matter will have a great number of positive spots resulting from free amino groups. Likewise, individual clay crystals, having a cation-exchange capacity, will have

[1] Contribution from the division of soil physics, department of agronomy, University of Illinois, Urbana, Illinois. Published with the approval of the director of the experiment station.

[2] Assistant in agricultural chemistry, University of Idaho, Moscow, Idaho.

[3] Assistant chief in soil physics.

a great number of negative spots. If the two particles should orient themselves in such a manner that there was a mutual attraction between many of these spots, a stable combination would be obtained. In this way the clay crystal might be covered by a "network" of organic material.

In the present study, albumen-montmorillonite and gelatin-montmorillonite complexes were prepared. The reactions were followed by measuring the change in the (001) spacings of the montmorillonite by x-ray diffraction methods. Montmorillonite was selected for this study because this type of mineral is one of the components of many of the clays possessing a high cation-exchange capacity. Proteins were selected because they are one of the most common of the nitrogenous substances added to soils.

EXPERIMENTAL TECHNIC

The montmorillonite was obtained by taking a fraction of Wyoming bentonite containing those particles less than 0.5 μ in diameter. The water suspension of this fraction was raised to approximately pH 10 by adding sodium hydroxide. Water suspensions of albumen and of gelatin were made and adjusted to the same pH by the same method. The concentration of the suspensions was determined by drying known volumes in an oven at 105°C. The first step in the preparation of the protein-montmorillonite complexes was the thorough mixing of an alkaline protein suspension with an alkaline montmorillonite suspension. In alkaline suspension, both the montmorillonite and the protein are negatively charged, with the result that the two substances are not mutually attracted to any great extent. Under these conditions a homogeneous mixture is easily obtained. The final step in the preparation of the complex was the acidification of the mixed suspension. The montmorillonite remains negatively charged while the protein becomes positively charged when the pH of the suspension becomes lower than its isoelectric pH. Under these final conditions the protein and montmorillonite mutually attract each other and are completely flocculated. All of the suspensions were acidified gradually by adding dilute acetic acid. This was followed by adding concentrated acetic acid where low pH values were desired. The acidified suspensions were shaken in a mechanical shaker for 48 hours. The flocculated protein-montmorillonite complexes were then filtered, washed with water, and dried over anhydrous magnesium perchlorate.

Three series of protein-montmorillonite samples were prepared. In one series the amount of gelatin per gram of montmorillonite was varied. In this series, the final pH of the mixed suspensions was adjusted to 2.6. In a second series, the amount of albumen per gram of montmorillonite was varied, and the final pH of the suspension was adjusted to 2.6. In the third series, 1 gm. of gelatin was added to each gram of montmorillonite in the suspension. In this series, the final pH of the suspension was varied.

A powder x-ray diffraction pattern was made from each of the dried samples. The samples were exposed in a closed system over anhydrous magnesium

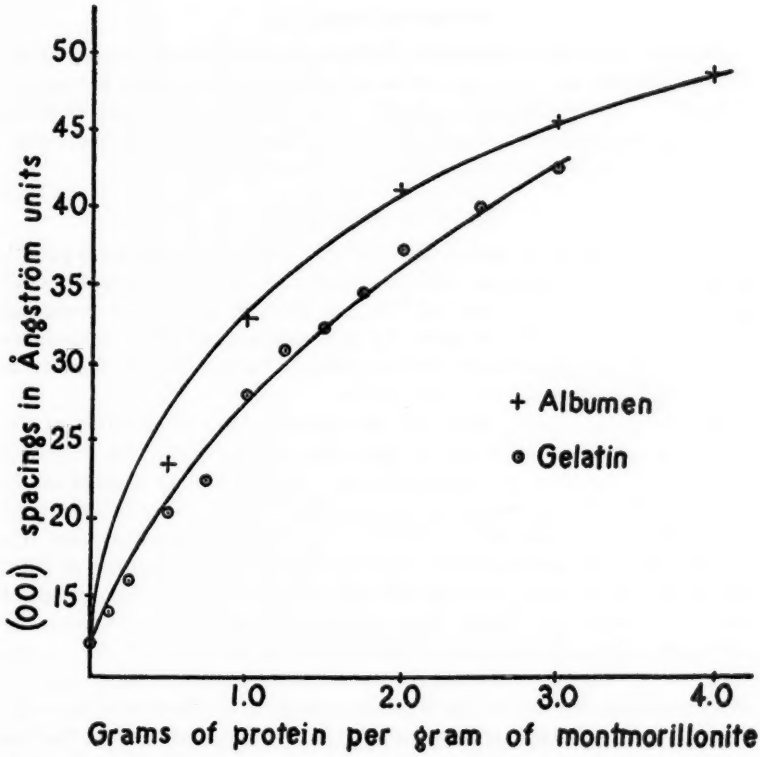

FIG. 1. EFFECT OF VARIOUS AMOUNTS OF ADSORBED PROTEINS ON THE (001) SPACINGS OF MONTMORILLONITE

TABLE 1

Effect of hydrogen-ion concentration on the adsorption of gelatin by montmorillonite

FINAL pH OF THE SUSPENSION DURING PREPARATION	(001) SPACINGS OF MONTMORILLONITE TREATED WITH GELATIN*
	Å.
7.0	23.0
5.5	25.7
4.0	27.0
2.7	26.9
1.0	26.9

* 1 gm. gelatin to 1 gm. montmorillonite.

perchlorate. FeKα radiation was used. The diffracted radiation was recorded on a flat film at a distance of 5 cm. from the sample.

EXPERIMENTAL RESULTS

The (001) spacings of montmorillonite samples treated with varying quantities of albumen and those of another series treated with gelatin are plotted in figure 1. X-ray diffraction patterns of the gelatin-montmorillonite series are reproduced in plate 1. The effect of the hydrogen-ion concentration on the adsorption of gelatin by montmorillonite is shown in table 1.

DISCUSSION OF RESULTS

The data presented in figure 1 and the x-ray diffraction diagrams in plate 1 show that the (001) spacings and the intensity of diffraction from the (001) planes of montmorillonite gradually increase upon the addition of increasing amounts of protein. This change in the (001) spacings and (001) planes shows that the large protein molecules are being adsorbed within the variable portion of the (001) spacing of the crystal lattice.

The results in table 1 show that the hydrogen-ion concentration of the suspensions during preparation is important in determining the degree of adsorption of proteins by montmorillonite. The adsorption is more nearly complete when the hydrogen-ion concentration is high. This indicates that the protein is being adsorbed as cations. The high hydrogen-ion concentration results in an increase in the degree of ionization of the amino or basic groups and at the same time represses the ionization of the acidic groups of the protein molecules. Under these conditions the amphoteric protein molecule tends to act as a cation, and the tendency to act as an anion is diminished.

In order to determine more of the nature of the adsorption of proteins by montmorillonite, the adsorption of gelatin treated with nitrous acid was compared to the adsorption of untreated gelatin. Nitrous acid destroys the free amino groups of proteins, thereby rendering them non-basic. In this experiment 1 gm. of gelatin was added to 1 gm. of montmorillonite in each case. The montmorillonite complex with untreated gelatin had a (001) spacing 8.0 Å. greater than the complex with the nitrous acid treated gelatin. The treated gelatin was still polar, and for this reason showed evidence of adsorption by the montmorillonite; but the untreated gelatin, which was capable of reacting as a cation, was more completely adsorbed.

SUMMARY

X-ray diffraction data obtained in this investigation show that albumen and gelatin are adsorbed within the characteristic expansible portion of the montmorillonite crystal lattice. These proteins are more completely adsorbed in suspensions with high hydrogen-ion concentrations than in suspensions with low hydrogen-ion concentrations. Untreated gelatin was more completely adsorbed than gelatin treated with nitrous acid to destroy its basic properties. These observations suggest that the adsorption of proteins as cations is partly responsible for their combinations with montmorillonite.

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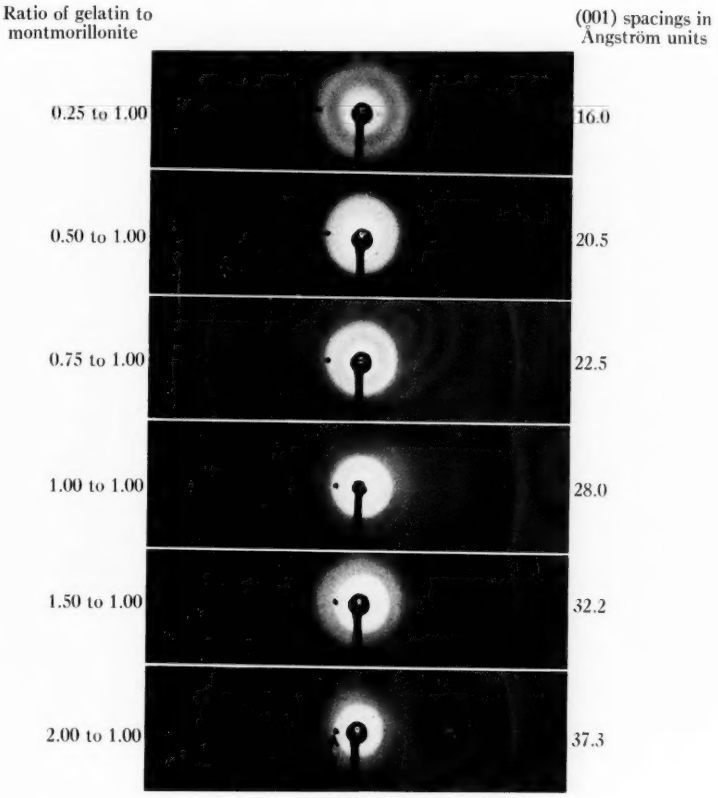
PLATE 1

X-RAY DIFFRACTION DIAGRAMS OF SAMPLES OF MONTMORILLONITE TREATED WITH VARIOUS AMOUNTS OF GELATIN IN SUSPENSIONS ADJUSTED TO pH 2.6


Ratio of gelatin to montmorillonite
(001) spacings in Ångström units
0.25 to 1.00
16.0
0.50 to 1.00
20.5
0.75 to 1.00
22.5
1.00 to 1.00
28.0
1.50 to 1.00
32.2
2.00 to 1.00
37.3
(001) diffraction line

DISPERSION OF LATERITIC SOILS AND THE EFFECT OF ORGANIC MATTER ON MECHANICAL ANALYSIS[1]

O. W. BEALE[2]

U. S. Department of Agriculture

Received for publication August 14, 1939

One of the important physical determinations made in connection with studies of soil erodibility is the mechanical analysis. In making mechanical analyses of lateritic soils some difficulties were experienced in obtaining complete dispersion, a fact which led to an investigation of the effectiveness of different dispersing agents. It was also observed that most of these soils contained very little organic matter; it was thought advisable, therefore, to test the effect of omitting the hydrogen peroxide pretreatment for removing organic matter in order that this time-consuming operation might be eliminated in routine work if it was found to be unnecessary.

DISPERSION OF SOILS

The dispersion of lateritic soils was studied after flocculation was encountered during mechanical analysis when sodium oxalate was used as the deflocculent. Alexander (1), noting that the clay fraction of lateritic soils dispersed with sodium oxalate frequently flocculated, suggested that in such cases sodium hydroxide be used in making mechanical analyses. He found no indication of flocculation in sodium hydroxide suspensions after these samples had been allowed to stand for 4 weeks. The results obtained in this laboratory also showed that sodium oxalate suspensions were very unstable. The principal disadvantage of using sodium hydroxide alone is the difficulty of making an accurate correction for the weight of dispersing agent present in the suspension. The value for the correction varies considerably from one determination to another, although the same concentration of sodium hydroxide is used.

Steele and Bradfield (7) dispersed soils with sodium oxalate alone and with sodium hydroxide alone after removing the bases by electrodialysis, and showed that the clay content was higher in the soils dispersed with sodium oxalate. Bouyoucos (2) dispersed soils with a combination of sodium oxalate and sodium hydroxide

Preliminary tests showed that satisfactory dispersion was obtained by using 5 ml. of 0.5 *N* $Na_2C_2O_4$ and 3 ml. of *N* NaOH per liter of suspension containing

[1] Contribution of the Soil Conservation Service in cooperation with the South Carolina Agricultural Experiment Station.

[2] Junior soil technologist, Soil Conservation Service, Division of Research, Clemson S. C.

10 gm. of soil (plate 1). This combination gave stable suspensions, and the variation of the correction for the weight of dispersing agent present in the suspension was very small. Blanks to determine the correction for the weight of dispersing agent always gave approximately the same values, which were relatively close to the theoretical values.

Table 1 shows the mechanical analyses of some lateritic soils dispersed with sodium oxalate alone and with the combination of sodium oxalate and sodium hydroxide. Comparisons of the clay contents obtained clearly show that flocculation occurred in several of the samples dispersed with sodium oxalate. The B horizons of most samples apparently flocculated more readily than the A horizons when sodium oxalate was used alone. The silt fractions show a marked decrease and the clay fractions a large increase when the flocculated

TABLE 1

Mechanical analyses of lateritic soils dispersed with sodium oxalate alone and with combined sodium oxalate and sodium hydroxide

SOIL TYPE	HORIZON	DISPERSED USING 10 ML. 0.5 *N* $Na_2C_2O_4$			DISPERSED USING 5 ML. 0.5 *N* $Na_2C_2O_4$ + 3 ML. *N* NaOH		
		Sand	Silt	Clay	Sand	Silt	Clay
		per cent	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*
Cecil sandy clay loam.....	B	31.61	10.92	59.25	30.51	9.35	61.41
Cecil sandy clay loam.....	B	34.05	53.25	15.36*	33.73	11.76	56.02
Cecil sandy loam.....	B	32.79	15.26	44.25*	33.36	11.10	57.33
Cecil sandy clay loam.....	B	36.46	66.04	3.36*	33.51	12.09	55.52
Cecil sandy loam.....	B	25.30	12.10	64.72	24.83	10.86	65.41
Cecil sandy loam.....	A	76.63	13.39	10.64	75.84	11.44	12.21
Cecil sandy loam.....	A	88.67	8.02	6.41	85.49	8.41	6.81
Cecil sandy loam.....	B	47.96	10.32	43.71	47.40	9.32	44.58
Cecil sandy loam.....	B	40.26	13.65	48.17*	38.92	11.49	50.38

* Visible flocculation occurred during sedimentation in less than 8 hours.

samples were dispersed with the mixture of sodium oxalate and sodium hydroxide instead of the sodium oxalate alone.

Mechanical analyses have been made on about 200 samples of lateritic soils dispersed with the mixture of sodium oxalate and sodium hydroxide, and the results have been very satisfactory.

EFFECT OF ORGANIC MATTER

The necessity of eliminating the organic matter by pretreating the soil with hydrogen peroxide, as a preliminary step to mechanical analysis, was questionable. This pretreatment tends to make the procedure for mechanical analysis long and tedious. Hydrogen peroxide treatment and the number of washings necessary to free the soil of organic matter brought into solution by the peroxide limited the number of analyses to eight samples in duplicate a week. By

omitting the peroxide treatment and subsequent washings, the number of analyses which could be made during a week was more than trebled.

In making mechanical analyses of heavy alkaline soils, Joseph and Snow (4) omitted both the hydrochloric acid and the hydrogen peroxide pretreatments. They reported results on soils of high organic matter and high calcium carbonate content, and concluded that no soils encountered had required the removal of the organic matter.

Robinson (6) showed that in order to break down the mineral particles cemented together by the organic matter, it was necessary to pretreat soils to remove the organic matter. He found that in every case when the organic material was oxidized, the amount of clay and the degree of dispersion of the soils were increased.

The action of H_2O_2 on weathered mica was studied by Drosdoff and Miles (3). The result of the hydrogen peroxide treatment on weathered mica of the unhydrated type showed that the larger pieces were disintegrated, thereby increasing the amount of finer material and decreasing the coarser fractions. Mechanical analyses of soils high in mica content would probably be affected significantly.

Two methods of mechanical analysis of soils were adopted by the First International Soil Science Congress (8). One of these incorporated the hydrogen peroxide pretreatment to remove organic matter, and the other omitted it.

Data presented in table 2 show a comparison of results obtained when soils were pretreated with hydrogen peroxide and when the pretreatment was omitted. The pipette method was used in making the mechanical analysis, based on the procedure outlined by Olmstead, Alexander, and Middleton (5). The sand fraction was determined by difference when the method omitted the hydrogen peroxide pretreatment; and the sand fraction was weighed when the method included pretreatment.

All samples used were acid, having pH values between 4.65 and 6.63. The pH values were obtained by the glass electrode method. An attempt to correlate pH values with the quantity of dispersing agent required was not successful. Organic carbon was determined by dry combustion, and the percentage of carbon was multiplied by the factor 1.724 to obtain the values listed as percentage of organic matter. As the solution loss is not shown in table 2, a discrepancy may be noted when the percentages of sand, silt, and clay fractions for some samples treated with hydrogen peroxide are totaled. In some samples pretreated with H_2O_2, however, it was noted that instead of a solution loss a slight gain in weight occurred. The sand fraction includes particles of 2.0 to 0.02 mm., the silt fraction 0.02 to 0.002 mm., and the clay fraction 0.002 mm. and smaller.

A comparison of the clay contents obtained by the two methods shows that they closely approach the same values. All values reported are averages of duplicates, which in no instance differed by more than 1 per cent. The mean difference between treatments shows that the values for the hydrogen peroxide

treated samples are slightly higher than the untreated samples, indicating that pretreatment with hydrogen peroxide does affect the amount of clay obtained.

TABLE 2

Comparison of mechanical analysis of lateritic soils with and without hydrogen peroxide pretreatment

SOIL TYPE	HORIZON	ORGANIC MATTER (C × 1.724)	SAND		SILT		CLAY	
			H_2O_2 Treated	H_2O_2 Omitted	H_2O_2 Treated	H_2O_2 Omitted	H_2O_2 Treated	H_2O_2 Omitted
		per cent	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*
Cecil sandy loam	A	0.79	84.74	85.43	7.79	6.91	7.38	7.66
Cecil sandy loam	B	0.74	47.96	47.83	8.16	8.51	44.06	43.66
Cecil sandy clay loam	A	1.55	65.96	66.28	12.03	11.56	22.05	22.16
Cecil sandy clay loam	B	0.84	32.26	32.00	6.62	6.84	61.85	61.16
Cecil sandy clay loam	A	0.95	62.44	63.75	10.76	9.64	26.71	26.61
Cecil sandy clay loam	B	0.48	32.51	35.14	12.98	11.27	55.46	53.58
Cecil sandy loam	A	1.07	72.02	72.27	14.43	15.27	12.29	12.46
Cecil sandy loam	B	0.64	32.75	32.31	11.27	10.57	57.11	57.13
Cecil sandy loam	A_1	0.57	89.61	90.38	5.99	6.09	3.87	3.53
Cecil sandy loam	A_2	0.45	72.39	71.16	16.31	17.31	12.33	11.54
Cecil sandy loam	B	0.43	39.04	39.73	11.76	10.96	50.29	49.32
Cecil sandy clay loam	A	0.76	72.21	72.77	7.96	6.61	20.47	20.62
Cecil sandy clay loam	B	0.33	34.96	33.25	12.48	12.47	54.42	54.28
Cecil sandy loam	A	2.38	74.84	76.02	12.29	12.93	10.37	11.05
Cecil sandy loam	B	1.07	25.60	25.67	10.03	10.10	64.67	64.23
Cecil sandy loam	A	1.59	80.06	81.22	10.32	11.34	8.26	7.44
Cecil sandy loam	A	0.95	83.22	83.79	10.52	8.70	7.10	7.51
Cecil sandy loam	B	0.86	46.08	46.13	10.25	11.92	43.61	41.95
Cecil sandy loam	A	0.81	84.57	85.14	7.41	7.33	7.99	7.53
Cecil sandy loam	B	0.72	56.27	56.24	13.27	13.06	31.97	30.70
Susquehanna clay loam	A	2.62	53.51	55.52	12.38	10.27	36.50	34.21
Susquehanna clay loam	B	1.00	34.86	35.23	11.27	8.70	57.84	56.07
Greenville sandy loam	A	1.22	56.70	60.96	2.37	3.73	41.47	35.31
Greenville sandy loam	B	0.90	42.85	42.54	2.71	3.75	55.33	53.71
Orangeburg sandy loam	A	0.57	84.15	85.51	6.19	5.16	10.39	9.33
Orangeburg sandy loam	B	0.31	70.58	71.99	7.34	6.20	23.61	21.81
Ruston sandy loam	A	0.72	90.65	91.44	4.31	4.58	4.86	3.98
Ruston sandy loam	B	0.33	70.27	70.03	8.19	7.59	23.28	22.38
Iredell loam	A	1.52	63.70	65.83	19.82	19.21	16.38	14.96
Iredell loam	B	0.76	29.15	27.55	13.57	12.45	57.56	59.94
Davidson clay loam	A	1.98	53.96	57.05	15.88	15.45	29.44	27.49
Davidson clay loam	B	0.93	40.66	42.59	15.81	14.83	44.26	42.58
Mean difference between treatments				0.69		−0.35		−0.85
Standard error of mean differences				±0.23		±0.18		±0.24

There is apparently no definite relation between the organic matter content and the difference in clay values obtained by the two methods. The organic matter contents range from 0.33 to 2.62 per cent. Some samples with organic

matter above 1 per cent give, by both methods, results very close to the same values. Other samples which contain less organic matter show results more widely separated.

The mechanical analysis of most lateritic soils for practical purposes can probably be made by the method in which the hydrogen peroxide pretreatment is omitted, thereby saving much time. The thirty-two samples shown in table 2 were analyzed in less than a week when the pretreatment was omitted, whereas more than a month was required when they were pretreated with hydrogen peroxide. The omission of the hydrogen peroxide pretreatment is recommended for routine mechanical analyses on most lateritic soils.

SUMMARY

Flocculation occurred during mechanical analysis of some lateritic soils dispersed with sodium oxalate. The result was that the values obtained for the clay fractions were far too low. Stable suspensions were obtained by using a mixture of 5 ml. 0.5 *N* $Na_2C_2O_4$ and 3 ml. *N* NaOH.

The effect of organic matter on mechanical analysis was studied. Data presented on 32 samples of lateritic soils show that the clay contents are slightly higher when the organic matter is removed, the silt fractions are not significantly different, and the sand fractions of the samples untreated are higher. In view of the time and work saved and the small difference between the two methods, it is concluded that the hydrogen peroxide pretreatment may be omitted for routine analyses of lateritic soils.

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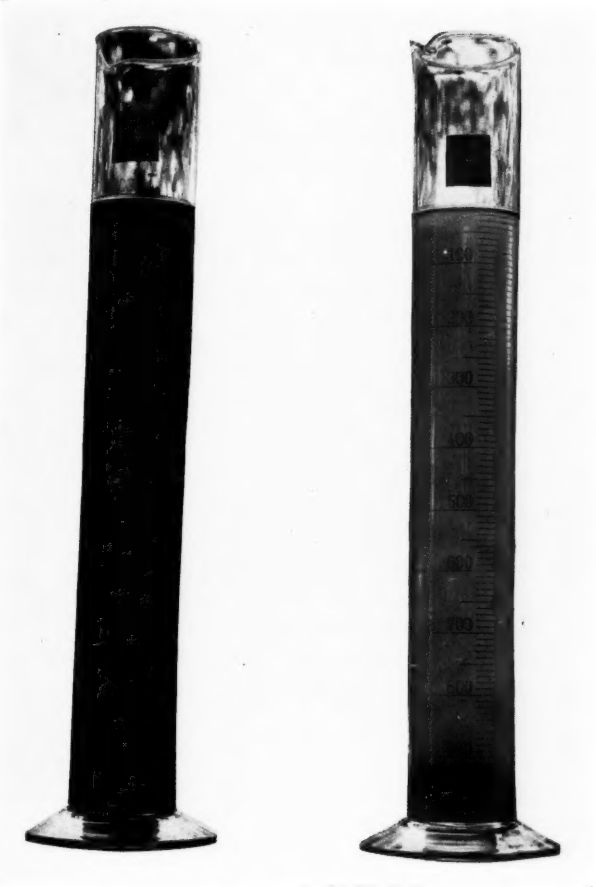
PLATE 1

DISPERSION OF CECIL SANDY CLAY LOAM

The soil in cylinder 1 was dispersed with sodium oxalate plus sodium hydroxide; that in cylinder 2, with sodium oxalate only. Flocculation was visible in cylinder 2 after 1 hour of sedimentation. The photograph was made after 18 hours.



THE GENESIS OF DAVIDSON CLAY LOAM

F. HARDY AND G. RODRIGUES

Imperial College of Tropical Agriculture, Trinidad, B.W.I.

Received for publication May 18, 1939

In our detailed investigations of the course of the changes between parent basic igneous rocks and their derived red earth soils, by means of silicate analysis and the application of dye tests [including our alizarin test (4)], representative samples of Davidson clay loam were examined along the lines of previous investigations into red earth formation in British Guiana (5) and Grenada (6). These samples, from a profile site in Chatham County, 50 miles west of Raleigh, North Carolina, are representative of (i) the parent rock at the 6-foot depth, (ii) its weathering crust, and (iii) the B horizon, or red earth, between the 20- and 24-inch depth, presumably derived from this weathered material.[1]

DESCRIPTION OF THE SAMPLES

(i) The *parent rock* is a fine-grained dolerite (diabase) or basalt consisting of about equal parts of intercrystallized white basic feldspar, probably anorthite, and dark bluish green ferromagnesian minerals, probably mainly pyroxene. Magnetite and quartz are scarce or absent, but ilmenite is present in small amount. The pyroxene, in part, may be a titan-augite, because the total quantity of titania seems to be too great to be accounted for solely by ilmenite. The unaltered rock occurs as deep-seated boulders and comprises kernels of all sizes, resulting from "onion-weathering" of the parent lava. The outer parts of the boulders split readily into a series of concentric layers, more or less decomposed.

(ii) The *weathering crust* or outermost shell, 5 to 8 mm. thick, is a coherent, structureless, brittle, lemon-yellow, sandy material, which easily crumbles. It merges imperceptibly with the red earth in which the decomposing boulders are embedded.

(iii) The *red earth*, comprising the *B horizon*, is described in the Soil Survey Bulletin for Chatham County (7) as a "dark red or maroon, heavy, stiff but brittle, smooth clay," which "breaks into large angular pieces which readily break into small angular particles."

Davidson clay loam was selected in 1930 by Middleton (9) for full laboratory

[1] The writers wish to thank J. F. Lutz, associate professor of soils, North Carolina State State College of Agriculture, Raleigh, N. C., for procuring material of the Davidson profile and for furnishing notes describing some of its features.

study as an example of a nonerosive soil. He describes the A horizon as reddish brown clay loam, 0 to 9 inches; the B_1 horizon, 9 to 36 inches, deep red, heavy brittle clay, breaking into large lumps that crumble into smaller angular and subangular fragments; the B_2 horizon, 36 to 60 inches, paler red, friable clay, overlying the C horizon, which consists of ocher-yellow, black, and reddish brown decomposition products of the parent rock. The laboratory data published by Middleton include complete physical and chemical analyses of material from the different horizons, as well as their colloidal components. Data appertaining to the chemical composition of the Davidson profile were also published by Anderson and Byers in 1931 (1) and discussed by them later in relation to soil classification (3). Colloidal fractions, four in number, were separated from the B_1 horizon material and chemically analyzed by Brown and Byers of the U. S. Bureau of Soils, who published their results in 1932, together with data for the fine and coarse silt fractions (2). The analytical results obtained by the Bureau of Soils investigators have been brought together and discussed by Marbut (8, p. 61, 62).

The climatic conditions now existing in the Southeastern States where Davidson clay loam has developed are subtropical, and the original vegetation was deciduous forest. The mean annual temperature is 60°F., the mean summer temperature 77°F., and the mean winter temperature 42°F.; the average annual rainfall is 44 inches, and the rain is fairly uniformly distributed throughout the year, though slightly greater in amount during the summer months.

DISCUSSION OF EXPERIMENTAL RESULTS

The same methods of examination were employed as those described fully in an article (6) on the red earth of Grenada, British West Indies. The results of chemical analysis are presented in table 1. The contents of quartz (determined by a tri-acid digestion method) are given separately from those of combined silica, and of free (gibbsitic) alumina (determined by the improved alizarin method) separately from those of combined alumina; similarly for the water of constitution of gibbsite as distinct from that of other hydrous minerals. This modification of the conventional method of presentation, by eliminating *free* oxide components, imparts much greater meaning to silica-alumina (and other) molecular ratios. Both the whole material and the colloidal clay fraction (2μ downward) were chemically analyzed. Comparable data obtained by the Bureau of Soils investigators are also presented in table 1.

The losses and gains of each oxide component are shown in table 2, *total alumina being assumed to remain constant* throughout the transformations between rock and red earth. Computations from the data of the Bureau of Soils investigators are also given for comparison, but the composition of the weathering crust is not included in these data, since this material was not analyzed by those investigators; instead, the results of our analysis of the crust are employed for evaluating the changes between the crust and the C horizon of the soil.

TABLE 1

Bulk chemical composition of the Davidson red earth profile samples

SAMPLE	PERCENTAGE COMPOSITION										MOLECULAR RATIOS*			
	SiO_2		Al_2O_3		Fe_2O_3	TiO_2	CaO	MgO	H_2O		$\frac{SiO_2}{Al_2O_3}$	$\frac{Fe_2O_3}{Al_2O_3}$	$\frac{SiO_2}{H_2O}$	$\frac{Al_2O_3}{H_2O}$
	Quartz	Combined	Gibbsitic	Combined					Gibbsitic	Other				
	Whole material†													
(i) Rock	....	52.0	...	15.9	14.5	1.9	7.1	4.2	...	2.1	5.55	0.58	7.41	1.33
(ii) Crust	(15.0)	(26.7)	7.3	8.8	25.9	3.0	0.6	3.2	3.9	3.8	(5.15)	1.87	(2.11)	0.41
(iii) B Horizon	5.8	34.0	3.1	24.1	19.5	1.8	0.2	0.4	1.6	10.2	2.40	0.52	1.00	0.42
	Colloidal clay (2 μ downward)													
(ii) Crust	1.1	23.1	10.7	14.4	32.2	1.4	tr.	0.8	5.7	8.7	2.73	0.70	1.26	0.29
(iii) B Horizon	0.4	33.0	7.0	22.8	21.6	1.4	tr.	0.5	3.7	8.9	2.47	0.60	1.11	0.45
Analysis by U. S. D. A., Bureau of Soils														
	Whole material													
C Horizon	....	52.6	21.0		13.4	1.2	0.3	1.0	9.2		4.26	0.41	1.89	0.44
B_2 Horizon	....	50.5	23.1		14.9	1.5	0.3	0.6	9.4		3.73	0.41	1.78	0.48
B_1 Horizon	....	52.7	22.9		10.6	1.4	0.5	0.4	10.6		3.92	0.30	1.67	0.42
A Horizon	....	70.5	12.5		6.1	1.8	0.8	0.5	7.7		9.28	0.31	2.86	0.31
	Colloidal clay (1 μ downward)													
C Horizon	....	35.2	29.7		20.1	0.9	0.5	0.1	12.5		2.02	0.43	0.96	0.48
B_2 Horizon	....	35.4	29.4		20.6	1.0	0.4	0.4	12.3		2.04	0.45	0.98	0.48
B_1 Horizon	....	36.9	31.7		16.0	0.9	0.6	0.4	13.1		1.98	0.32	0.97	0.49
A Horizon	....	34.4	32.1		12.4	2.0	0.6	0.9	17.1		1.82	0.25	0.73	0.40
Kaolinite	....	....	....		....	...	...	...	....		2.00	....	1.00	0.50

* Combined components (analysis by authors) and total components (analysis by U. S. D. A. Bureau of Soils).

† Sample (i), (ii), and (iii) were found to contain 0.024, 0.17, and 0.14 per cent MnO_2 respectively.

TABLE 2

Transformations between parent rock and weathering products of the Davidson profile

Compositions recalculated to constant total alumina

	ANALYSIS BY AUTHORS					ANALYSIS BY U. S. D. A., BUREAU OF SOILS INVESTIGATORS							
	Percentage Composition			Losses or Gains		Percentage Composition				Losses or Gains			
	(i) Rock	(ii) Crust	(iii) B Horizon	(ii) Crust	(iii) B Horizon	C Horizon	B_2 Horizon	B_1 Horizon	A Horizon	C Horizon*	B_2 Horizon	B_1 Horizon	A Horizon
		Whole material											
Quartz	....	(15.0)	3.4	+15.0	−11.6	39.8	34.7	36.6	89.6	−1.4	−5.1	+1.9	+53.0
Combined SiO_2	52.0	(26.2)	19.9	−25.8	−6.3								
Gibbsite	....	7.2	1.8	+7.2	−5.4	15.9	15.9	15.9	15.9	.....	.....	.....	.....
Combined Al_2O_3	15.9	8.7	14.1	−7.2	+5.4								
Fe_2O_3	14.5	25.6	11.4	+11.1	−14.2	10.1	10.3	7.4	7.8	−15.5	+0.2	−2.9	+0.4
TiO_2	1.9	3.0	1.1	+1.1	−1.9	0.9	1.0	1.0	2.3	−2.1	+0.1	0.0	+1.3
CaO	7.1	0.6	0.1	−6.5	−0.5	0.2	0.2	0.3	1.0	−0.4	0.0	+0.1	+0.7
MgO	4.2	3.2	0.2	−1.0	−3.0	0.8	0.4	0.3	0.6	−2.4	−0.4	−0.1	+0.3
H_2O													
Gibbsitic	....	3.8	0.9	+3.8	−2.9	7.0	6.5	7.4	9.8	−0.6	−0.5	+0.9	+2.4
Other	2.1	3.8	6.0	+1.7	+2.2								
Totals	97.7	97.1	58.9	−0.6	−38.2	74.7	69.0	68.9	127.0	−22.4	−5.7	−0.1	+58.1
		Colloidal clay											
Quartz	....	0.7	0.2	+0.7	−0.5	18.9	19.1	18.5	17.0	+3.6	+0.2	−0.6	−1.5
Combined SiO_2	52.0	14.6	17.6	−37.4	+3.0								
Gibbsite	....	6.8	3.7	+6.8	−3.1	15.9	15.9	15.9	15.9	.....	.....	.....	.....
Combined Al_2O_3	15.9	9.1	12.2	−6.8	+3.1								
Fe_2O_3	14.5	20.4	11.5	+5.9	−8.9	10.8	11.1	8.0	6.1	−9.6	+0.3	−3.1	−2.0
TiO_2	1.9	0.9	0.8	−1.0	−0.1	0.5	0.5	0.5	1.0	−0.4	0.0	0.0	+0.5
CaO	7.1	tr.	tr.	−7.1	0.0	0.3	0.2	0.3	0.3	+0.3	−0.1	+0.1	0.0
MgO	4.2	0.5	0.2	−3.7	−0.3	0.0	0.2	0.2	0.5	−0.5	+0.2	0.0	+0.3
H_2O													
Gibbsitic	...	3.6	2.0	+3.6	−1.6	6.7	6.7	6.6	8.5	−2.4	0.0	−0.1	+1.9
Other	2.1	5.5	4.8	+3.4	−0.7								
Totals	97.7	62.1	53.0	−35.6	−9.1	53.1	53.7	50.0	49.3	−9.0	+0.6	−3.7	−0.8

* From weathering crust.

By analogy with the British Guiana and the Grenada material, the weathering crust of the Davidson profile should be primary laterite. Insofar as this material contains free alumina (over 7 per cent) and a large amount of water of hydration (8 per cent) and is deficient in bases, it may tentatively be so regarded. The data in tables 1 and 2 reveal the changes that accompany the formation of (*a*) the weathering crust from diabase and (*b*) red earth from the crust, under the climatic conditions that have obtained in North Carolina.

Primary laterite formation

The development of the weathering crust from the parent rock evidently has been accompanied by a *loss of bases* and of *total silica*. The feldspar of the rock has apparently suffered complete decomposition, and part of its alumina has separated as crystalline *gibbsite* ($Al_2O_3 \cdot 3H_2O$). Consequently, a fixation of water of hydration has occurred. There has been an apparent gain in total iron oxide and titania, doubtless accounted for by losses of other components.

For the purpose of determining the mineralogical composition of the weathering crust, a sample was fractionated into the usual texture grades, and each sand fraction "cleaned" by the Truog sulfide-oxalate method (10). The component mineral grains after separation into "heavy" and "light" by sedimentation in bromoform were then identified under the microscope. The main results are given in table 3.

Nearly 86 per cent of the crust is comprised of sand particles over 10 μ in diameter. A considerable part of these consists of quartz, but the exact amount could not be determined because tri-acid digestion failed to break up completely the component silicate minerals; the treatment left a 27.1 per cent residue, of which 20.3 was removed by volatilization with hydrofluoric acid, though only about 15 per cent of this silica could be claimed as consisting of quartz.

The state of occurrence of iron oxide in the weathering crust was investigated by dye tests (6). The results are given in table 4.

From the results of the dye tests, the weathering crust evidently does not contain much free iron oxide, although it contains an appreciable quantity of active siliceous clay minerals.[2] Microscopical examination revealed the occurrence of large amounts (at least 50 per cent) of a *chloritic* mineral in the coarse and medium sand fractions of the weathering crust. This chlorite settled but slowly in bromoform, and sharp separation was not obtained; its specific gravity thus ranged between 2.8 and 2.9. Chemical analysis of a

Totals.....	97.7	62.1	53.0	−35.6	−9.1	53.1	53.7	50.0	49.3	−9.0	+0.6	−3.7	−0.8

* From weathering crust.

[2] *Diamine sky blue* is strongly adsorbed by free hydrous iron oxides from its solution in alcohol containing boric acid, but not from its solution in alcohol containing phosphate, because the phosphate is preferentially adsorbed and "blocks" the uptake of the dye. Under similar circumstances, halloysite strongly adsorbs diamine sky blue, but the presence of phosphate does not diminish its uptake. On the other hand, *janus red* is not appreciably adsorbed by hydrous iron oxides but is adsorbed markedly by the clay minerals. Hence it is possible, by these two dye tests, to differentiate between different clay minerals, in particular, between hydrous iron oxides and iron-bearing clay minerals or aluminosiliceous clay minerals.

sample of the portion that settled from the coarse sand fraction gave SiO_2, 25.9, Al_2O_3, 15.4, FeO, 16.4, Fe_2O_3, 11.4, TiO_2, 13.4, CaO, 0.9, MgO, 6.7, H_2O, 10.0—total 100.1 per cent. Expressed in molecular proportions, these

TABLE 3

Mineralogical composition of Davidson profile

Materials treated with H_2S and acid oxalate before examination*

	(i) PARENT ROCK	(ii) WEATHERING CRUST (LATERITE)	(iii) B HORIZON (RED EARTH)
	per cent	*per cent*	*per cent*
Texture analysis			
Coarse sand.....(> 200 μ)	48.8	45.4	3.3
Medium sand.....(200–50 μ)	27.6	14.6	7.3
Fine sand..... (50–10 μ)	19.6	25.7	25.4
Coarse silt.....(10–5 μ)	0.6	0.6	3.8
Fine silt + clay.....(< 5 μ)	3.4	13.7	60.2
Mineral separation (Bromoform: sp. gr. 2.85)			
Coarse sand: Heavy residue.....	(46.0)	41.8	5.3
Light fraction.....	(54.0)	58.2	94.7
Medium sand: Heavy residue.....	....	6.9	4.3
Light fraction.....	....	93.1	95.7
Fine sand: Heavy residue.....	....	0.1	0
Light fraction.....	....	99.9	100.0
Characteristic minerals			
Coarse sand: Heavy residue.....	Augite, ilmenite	Chlorite	Leucoxene, iron oxide concretions
Light fraction.....	Felspar and glass	Chlorite, quartz	Quartz
Medium sand: Heavy residue.....	Augite, ilmenite	Chlorite	Leucoxene, iron oxide concretions
Light fraction.....	Felspar and glass	Chlorite, quartz	Kaolinitic mineral chiefly Some quartz
Fine sand: Heavy residue.....	.....	(Nil)	(Nil)
Light fraction.....	.....	Quartz	Kaolinitic mineral

* Parent rock ground.

figures indicate a ferromagnesian mineral of formula $4(Mg \cdot FeO) \cdot 2Al_2Fe_2O_3 \cdot 4SiO_2 \cdot 5H_2O$, which is similar to that of the leptochlorite, delessite. The mineral occurs in the crust mainly as bright grass-green, clear, irregular grains.

Many of the grains contain abundant rusty decomposition products, and their surfaces are deeply etched. It has doubtless been formed by the decomposition of the augite component of the basic igneous rock.

The *colloidal clay* fraction ($<2\ \mu$) of the weathering crust is small in amount (less than 10 per cent), but its composition clearly indicates the nature of the further breakdown products, presumably derived in part from chlorite. It contains nearly 11 per cent of free (gibbsitic) alumina (16.4 per cent of gibbsite), but only 1 per cent of quartz (table 1). Its total iron oxide content is high (32.2 per cent), though only a relatively small amount of iron oxide appears to occur in the free state (diamine sky blue test, table 4). The clay stains heavily with janus red, indicating the presence of some active hydrous

TABLE 4

Results of dye tests on Davidson profile samples

Values in dye units absorbed per gram air-dry material

SAMPLE*	ALIZARIN UPTAKE†	DIAMINE SKY BLUE UPTAKE‡			JANUS RED UPTAKE
		Boric	Phosphatic	Difference§	
	Whole material				
(i) Rock	...	...	...	...	50
(ii) Weathering crust	72	106	42	50	199
(iii) B Horizon	30	528	202	265	988
	Colloidal clay				
(ii) Weathering crust	104	78	9	66	...
(iii) B Horizon	68	340	52	272	...

* All materials ground to pass a 100-mesh sieve.

† 1 gm. air-dry material ignited before dye test.

‡ By air-dry material.

§ Difference values corrected for dye uptake by phosphated halloysite.

clay mineral. In table 5 the mineralogical composition of the colloidal clay of the crust is computed in terms of secondary minerals.

Assuming all the combined alumina to occur as *kaolinite* ($Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O$), derived by the decomposition of the feldspar of the rock and amounting to 36.4 per cent of the weight of the colloidal clay, there still remains a residue (42.0 per cent) which presumably contains virtually all the iron oxide and the rest of the combined silica and water. Expressed in molecular proportions, the quantities of these constituents are as follows: Fe_2O_3, 0.201; SiO_2, 0.103; H_2O, 0.201; indicating an iron-bearing clay mineral of formula $2Fe_2O_3 \cdot SiO_2 \cdot 2H_2O$. This formula is not coincident with that generally accepted for hoeferite ($Fe_2O_3 \cdot 2SiO_2 \cdot 2H_2O$) nor with that for nontronite ($Fe_2O_3 \cdot 3SiO_2 \cdot 3H_2O$), but the fact that the ratios of $Fe_2O_3 : SiO_2 : H_2O$ are those of the simple whole numbers 2:1:2, suggests that the substance is a definite mineral, the identity

and specific properties of which need to be established by further study. It may have been produced either by the decomposition of chlorite or directly from augite.

Red earth formation

The formation of the red earth comprising the B horizon of the Davidson profile, assuming no loss of total alumina (table 2), has involved the removal of large amounts of silica, both free as quartz, and combined in siliceous min-

TABLE 5

Transformations between parent rock and colloidal clay products of the Davidson profile

Compositions recalculated to kaolinite

	PERCENTAGE COMPOSITION			LOSSES OR GAINS	
	Kaolinite (ideal formula)	Weathering crust	B horizon	Weathering crust	B horizon
Nonquartz SiO_2	46.6	63.9	57.0	+17.3	+10.4
Combined Al_2O_3	39.4	39.4	39.4	.....	.....
H_2O	14.0	23.8	15.4	+9.8	+1.4
Computation as minerals (assuming kaolinite formation)					
Crystalline components					
Gibbsite ($Al_2O_3 \cdot 3H_2O$)		16.4	10.7		
Kaolinite ($Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O$)		36.4	57.6		
Quartz (SiO_2)		1.1	0.4		
Iron mineral ($2Fe_2O_3 \cdot SiO_2 \cdot 2H_2O$)		42.0	0	Fe_2O_3, 32.2 SiO_2, 6.2 H_2O, 3.6	
Amorphous components					
Free iron oxides (Fe_2O_3)		0	21.6	Loss, 10.6	
Free silica (SiO_2)		0	6.2	From iron mineral	
Titania (TiO_2)		1.4	1.4	.....	
Bases (K_2O, Na_2O, CaO, MgO)		0.8	0.5	.....	
Water, excess (H_2O)		0	0.9	.....	
Total		98.1	99.3		

erals. Much of the gibbsite (nearly 60 per cent) has disappeared, presumably through its *resilication into a secondary kaolinitic mineral* (probably halloysite), by analogy with the transformations of primary laterite to kaolinitic red earth in British Guiana and Grenada (5, 6). A further loss of bases, especially magnesia, and a considerable loss of total iron oxide and titania (16 per cent), have also occurred.

The red earth contains only 36 per cent by weight of sand ($>10\ \mu$). More than 11 per cent of this sand is quartz, insoluble in tri-acid mixture. A large proportion (nearly 70 per cent) is crystalline halloysite or kaolinite, which is

deeply stained by janus red. Nearly 3 per cent of the particles rapidly settle in bromoform and consist mainly of black ilmenite, much altered into pale yellow, waxy *leucoxene*, giving a spotty appearance to the grains. Chemical analysis of a sample of heavy residue from the coarse sand fraction gave SiO_2, 13.9, FeO, 22.2, TiO_2, 63.1, CaO, 1.1—total 100.3 per cent. The rest of the heavy residue consists of tiny shotlike red concretions, probably hematite.

The state of occurrence of iron oxide in the red earth is entirely different from that in the weathering crust, as is clearly indicated by dye tests (table 4). Apparently nearly all of the oxide occurs as free red hydrous iron oxide, possibly mainly goethite.

The *colloidal clay* fraction ($<2\ \mu$) of the red earth comprises a large part of the whole material, probably over 50 per cent (1). It consists chiefly of halloysite or kaolinite (58 per cent), together with hydrous iron oxide (22 per cent), which imparts a bright red color to the material (table 5). It also contains about 10 per cent of gibbsite, or virtually all the free alumina of the whole material, in addition to nearly 7 per cent of free silica, of which only 0.4 per cent is quartz, the rest presumably being hydrous silica, and $1\frac{1}{2}$ per cent of free titania.

A sample of the colloidal clay fraction of the red earth was subjected to the Truog sulfide-oxalate treatment (10), and the resulting clay, which was nearly white, was chemically analyzed. It gave SiO_2, 36.8, Al_2O_3 (gibbsitic), 1.0, Al_2O_3 (combined), 30.3, Fe_2O_3, 9.5 per cent, having a silica-alumina molecular ratio of exactly 2.00, which is that of halloysite. The loss of iron oxide caused by the treatment was 68 per cent, and the loss of silica, 27 per cent. Most of the free alumina (gibbsitic) was removed by the treatment.

The Davidson red earth is very similar in composition to the Demerara and Grenada red earths, in that it consists essentially of secondary kaolinitic material (65 to 75 per cent), stained red with hydrous iron oxides (10 to 20 per cent), and containing secondary quartz (3 to 6 per cent), with some residual gibbsite (5 per cent). For purposes of comparison between the Grenada and the Davidson profiles, the mineralogical composition of the weathering crusts and that of the red earths have been computed and brought together in table 6.

Comparison with Bureau of Soils results

The clay mineral forming the main component of Davidson clay loam is believed by Brown and Byers (2) to be kaolinitic, solely on the grounds that the silica-alumina ratio of the colloidal fraction is very nearly 2.0 (see table 1). Their data do not show, however, a partition of total alumina into free and combined alumina, which the writers' analyses have proved to be feasible. Allowing for free (gibbsitic) alumina, the silica-alumina ratios are seen from our analyses actually to be *greater than* 2.0 (nearer 2.5 for the B horizon and 2.7 for the weathering crust), which suggests that the aluminosiliceous component is *anauxite* or some other silica-rich mineral of the kaolin group, unless it be granted that the surplus silica is present as free hydrous silica.

Anderson and Byers (1) describe the Davidson soil as "lateritic" on account of the low silica-*sesquioxide* ratios. The writers have elsewhere (6) discussed the nomenclature of rock-weathering products, and in accordance with our findings, we would use this term only for describing materials in which the presence of notable amounts of gibbsite (or other form of free alumina) had definitely been proved and not merely inferred. The alizarin test has directly demonstrated the presence of this essential component, both in the weathering

TABLE 6

Comparison of mineralogical composition of weathering crusts and red earths of the Grenada and Davidson profiles

Approximate percentage composition, estimated from the laboratory data

COMPONENT MINERALS	GRENADA PROFILE	DAVIDSON PROFILE
Weathering crust		
Gibbsite ($Al_2O_3 \cdot 3H_2O$)	39.1	11.2
Halloysite or kaolinite	29.3	10.0
Hydrous iron oxides	10.9	2.5
Secondary quartz	2.9	(15.0)
Hydrous silica	2.3	0.8
Titania (free)	2.6	0.5
Other minerals	12.9 (magnetite)	(53.0) (Chlorite) (1.8)? (Leucoxene) 5.2 (Iron-silicate clay mineral)
Total	100.0	100.0
Red earth		
Gibbsite ($Al_2O_3 \cdot 3H_2O$)	5.1	5.0
Halloysite or kaolinite	70.9	67.4
Hydrous iron oxides	11.2	15.8
Secondary quartz	2.9	6.2
Hydrous silica	0.0	3.3
Titania (free)	1.3	0.8
Other minerals	8.6 (magnetite)	1.5 (leucoxene)
Total	100.0	100.0

crust and in the red earth of the Davidson profile, the approximate contents being 11 and 5 per cent respectively, in contrast to 39 and 5 per cent for the Grenada profile (table 6). The weathering crust, although lateritic in nature, should not unqualifiedly be called "laterite," because its content of free alumina is slightly less than 13 per cent, and its silica-alumina ratio is greater than 1.33 (6). The occurrence in it of a preponderant amount of chlorite, the paucity of free iron oxide, and the presence of a considerable amount of quartz, may

perhaps justify the name "chloritic quartzose laterite." Judged by chemical composition (tables 1 and 2), the material is evidently not identical with the C horizon sample analyzed by the Bureau of Soils investigators, which closely resembles the red earth. Its formation from the parent rock has not been accompanied by appreciable losses of main constituents except bases, a fact which contrasts it markedly with the true laterite crust derived from basic igneous rocks in the humid tropics (0.6 per cent loss between rock and crust in the Davidson profile as against 38.2 per cent loss of total constituents in the Grenada profile). Its development has mainly involved an internal rearrangement of constituent oxides, with the formation of characteristic new iron-bearing minerals, of which one (chlorite) is a well-known secondary product and the other is an unidentified siliceous clay mineral.

The B horizon material of the Davidson profile, being almost identical with that of the Grenada profile, would briefly be called "red earth" (6). Because it contains gibbsite as well as abundant free hydrous iron oxide, it might alternatively be designated "lateritic ferruginous clay."

The Bureau of Soils analyses indicate that Davidson clay loam has begun to show profile differentiation. The very high silica-alumina ratio, 9.3, for the A horizon of the whole soil may be accounted for on the assumption that silica has accumulated in the surface soil, presumably as quartz. The colloidal clay fraction of the A horizon exhibits a low ratio, 1.8, and a normal content of silica. As quartz was not determined separately, this assumption is merely conjectural. Its acceptance would lead to the conclusion that the Davidson soil is *podzolized*. The ratios involving iron oxide also furnish evidence of surface leaching and demonstrate the removal of iron compounds from the A horizon and their accumulation in the B_2 horizon, though not in the B_1 horizon. Though the formation of the parent material of the Davidson soil has evidently taken place from below, upward (parent rock, weathering crust, C horizon clay), the development of the profile has proceeded by downward leaching under acidic humic conditions; it thus may be regarded as a tropical podzolic process. In the British Guiana red earth, (5) profile differentiation has proceeded to a very much greater extent, the A horizon consisting of a thick layer of highly quartzose residual sand, and the profile closely resembling that of a true podzol.

SUMMARY AND CONCLUSIONS

This investigation is an attempt to trace the mineralogical and chemical transformations that proceed during the development of Davidson red clay loam from basic igneous rock occurring in North Carolina lying within the Piedmont Region.

The quantitative methods employed were chemical analysis of whole materials and clay fractions both after fusion and after tri-acid digestion (for quartz), and alizarin adsorption after ignition (for free alumina). The qualitative methods were adsorption of other dyes for identifying free hydrous iron

oxides and siliceous clay minerals, and simple mineralogical examination of texture fractions.

Samples of (i) parent basic igneous rock, (ii) yellow weathering crust, and (iii) B horizon red earth subsoil were examined, and the results were compared with less complete data obtained by Bureau of Soils investigators.

The formation of the weathering crust from the rock, and of the red earth from the crust as deduced from the laboratory results, is fully described and discussed.

The *crust* is a sandy material consisting essentially of chlorite, secondary quartz, and halloysite, together with gibbsite, which indicates its lateritic nature. Its colloidal fraction (less than 10 per cent of the whole) contains an unidentified iron-bearing clay mineral of probable formula, $2Fe_2O_3 \cdot SiO_2 \cdot 2H_2O$. Its composition is contrasted with that of the laterite crust of decomposing basic igneous rocks occurring in British Guiana and Grenada which contains three times as much gibbsite and halloysite but no chlorite and much less quartz.

The *B horizon red earth* of the Davidson profile and of the British Guiana and Grenada profiles contains more than half its weight of colloidal matter and consists essentially of halloysite, stained red with free hydrous iron oxides, probably mainly goethite, together with some anhydrous hematite. It contains an appreciable amount of gibbsite and a little secondary quartz; the Davidson red earth also contains free hydrous silica.

The genesis of the halloysitic component of red earths is believed to be the resilication of gibbsite occurring in the weathering crusts, and chiefly derived from basic (lime-soda) feldspars occurring in the parent igneous rock.

The Davidson soil profile displays a partially podzolized A horizon, with slight accumulation of iron oxide in the B_2 horizon. Humid tropical red earth profiles usually display similar but much more pronounced differentiation; their A horizon in some instances consists almost entirely of residual quartz sand.

In order fully to trace the mineralogical and chemical transformations that occur during the genesis of red earths from basic igneous rocks, and to elucidate the processes involved in laterization and podzolization, the application of modified and additional methods of silicate analysis is urged, as well as the employment of dye tests, microscopical examination, and other simple laboratory methods. It is insufficient merely to determine the component oxides constituting rock-weathering products and soil profile horizons; differentiation should be made between those oxides which occur in the free (often hydrous) state and those which are combined.

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FACTORIAL DIAGRAMS

J. E. A. DEN DOOP

Bandoeng, Java, Dutch East Indies

Received for publication April 8, 1939

The term *factorial diagram* may denote a diagram of data resulting from some experiment with factorial design. Such data, which may be denoted as *factorial data* and which are measurements of some property, can be considered as a variable, depending on the factors as independent variables. Analytically, factorial data, as dependent on their factors, can be considered as a polydimensional system. The order of dimension equals the number of factors plus one. For a single factor such a system can be represented diagrammatically by a line in a flat plane. For two factors the straightforward diagram would be a three-dimensional structure in space, whereas for more than two factors the corresponding diagrams would be imaginary. For two and three factors special indirect diagrams have been proposed, but these will not be discussed here.

The author has used in his work for many years a method of indirect diagrams in a flat plane which is applicable to any number of factors. As this method may be useful to other experimental workers, it is described in this paper.

The method is illustrated by a field experiment with tapioca (*Manihot utilissima* Pohl) laid out on the north coast of West-Java in a red volcanic clay loam, which was known to be very deficient in potassium, appreciably less so in phosphorus, and much less so in nitrogen. The chief purpose of the experiment was to test the availability of the soil phosphorus. This point will not be considered further, as it is irrelevant to the present purpose. The data obtained for fresh-tuber weights and for dry-starch weights are utilized here for explaining the diagrammatical method under consideration.

The experiment, T.503 (the author's register number), was of straightforward factorial design with 3 potassium, 3 phosphorus, and 4 nitrogen levels, including for each factor a 0 level. The 36 treatments were not replicated, as the area of land of the quality desired was only just large enough for 36 minimum-sized plots. The 36 plots were randomized over the whole experimental area, i.e., without confounding. Table 1 gives the necessary information on the levels and on the forms and quantities of fertilizer applied. The levels are denoted in two ways; for example, the 1st nitrogen level can also be spoken of as the 0 level for nitrogen; the 2nd phosphorus level, as the single-phosphorus level; the 3rd nitrogen level, as the double-nitrogen level.

In this table the treatments are denoted each by three numbers, which denote by their *position* from left to right the factors: potassium, phosphorus, and nitrogen. This, and not the usual NPK sequence, has been chosen in correspondence with this particular sequence of the factors in the diagrams, as produced in this paper. The numbers themselves denote the relative levels of each of the factors: thus, 024 means the combination of the double-phosphorus level with the quadruple-nitrogen level in the absence of potassium.

Diagram 1 is that for the tuber yields. The diagram consists of 36 points, corresponding to the 36 treatment yields. The unit of ordinates is equal for all the yields, and the origin is identical for all the ordinates. Thus the yields are measured by their vertical distance from the axis of abscissas.

Matters are different regarding the abscissas. It will be seen in diagram 1 that between the yield points three different sorts of lines have been drawn; viz., 1 dotted line, 3 broken lines, and 9 full lines, corresponding with the potassium line, 3 phosphorus lines, and 9 nitrogen lines. From the yield

TABLE 1

Forms and quantities of fertilizer applied in experiment T.503

FERTILIZERS	POTASSIUM, IN FORM OF SULFATE OF POTASSIUM CONTAINING 90 PER CENT SULFATE			PHOSPHORUS, IN FORM OF DOUBLE SUPERPHOSPHATE CONTAINING 36 PER CENT P_2O_5			NITROGEN, IN FORM OF SULFATE OF AMMONIA CONTAINING 21 PER CENT N			
Levels.....	1st	2nd	3rd	1st	2nd	3rd	1st	2nd	3rd	4th
Relative-level denotation.....	0	1	2	0	1	2	0	1	2	4
Quantities of the forms per plant*	0	36	72	0	12	24	0	12	24	48

* The plants were spaced 3 by 3 feet.

point as in the axis of ordinates, i.e., the yield point of the 000 treatment, in short from the 000 point, originate the potassium line, the 1st phosphorus line, and the 1st nitrogen line. These three lines are ordinary yield diagrams for one factor in a flat plane, or regression lines of yield on the particular single-factor concerned. The formulas for these lines, which will easily be understood without further explanation, are: 000–100–200, 000–010–020, and 000–001–002–004.

Whereas for these three regression lines the unit of ordinates is identical, their units of abscissas, i.e., the abscissas for the single levels of the factors, are different for the different factors. The choice of these units is, in general, arbitrary, but to assure as little as possible intersecting of lines in the diagram, the units have been chosen thus: 1 nitrogen line equals 4 units of nitrogen abscissas, 1 unit of phosphorus abscissas equals 4 + 1 or 5 units of nitrogen abscissas, and 1 unit of potassium abscissas equals 5 + 5 + 4 + 1 or 15 units of nitrogen abscissas. Thus equal apparent-regressions for nitrogen, phosphorus, and potassium in the diagram correspond to real regressions,

which are in the ratio of 1/15 to 1/5 to 1. Within all the nitrogen lines, however, regressions are on an identical scale, and so within all the phosphorus lines; there is, of course, also only one scale of regression within the one potassium line.

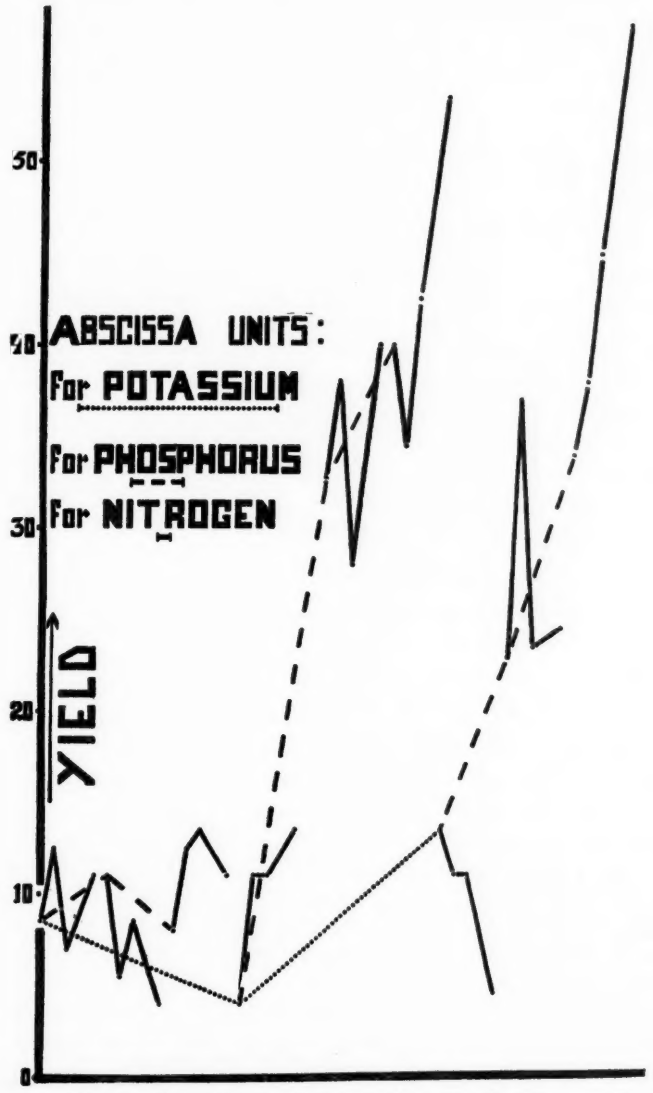

DIAGRAM 1. YIELD OF FRESH TAPIOCA ROOTS, IN TONS PER HECTARE, WITH DIFFERENT FERTILIZER TREATMENTS IN EXPERIMENT T.503

In diagram 1 will be noticed, besides the potassium line, the 1st phosphorus line, and the 1st nitrogen line, 2 further phosphorus lines, and 8 further nitrogen lines. Whereas the first 3 lines have an identical origin, all the other 10 lines have different origins. The formulas for the first 3 lines have already been given; those for the other 10 can easily be derived. For the 2nd phosphorus line, originating from the 100 point of the potassium line, for example, the formula can formally be derived from that of the 1st phosphorus line by adding to each member of the latter the numerical value of the point of origin of the former, as follows:

Formula of	1st phosphorus line	= 000 – 010 – 020
Formula of origin of	2nd phosphorus line	= 100 = 100 = 100
Formula of	2nd phosphorus line	= 100 – 110 – 120

In table 2 the derivations of all the lines of diagram 1 are to be found. As one nitrogen line contains 4 yield points, all the 9 nitrogen lines contain 36 yield points, i.e., all the yield points of the diagram. Thus in table 2 all the data on starch-yields and costs can be found after the formulas of the nitrogen lines. Some of these data are repeated after the formulas of the potassium and phosphorus lines, with a view to including in table 2 also for these lines the yield data in the sequence of their formulas.

With the aid of table 2 it is very simple to draw diagram 1. After having fixed the units of abscissas for the three factors, the potassium line, the 1st phosphorus line, and the 1st nitrogen line are drawn, the yield values for which are to be found in the correct order after their formulas in table 2. With the exception of their common origin, every yield point of these three lines is a point of origin for another nitrogen line, the yield data for which are also to be found in their correct order in table 2.

Graphically the three factors take a differential position in diagram 1, with the result that there is only one single line for potassium and that there are 3 lines for phosphorus and 9 for nitrogen. The position assigned to potassium may be denoted as the primary, that of phosphorus the secondary, and that for nitrogen the tertiary. If the primary position remains assigned to potassium but the positions for the other two factors are interchanged, the corresponding diagram will consist of 1 potassium line, 3 nitrogen lines, and 9 phosphorus lines. As the primary position can be assigned to every one of the three factors and in each case the other two factors can be interchanged, 6 diagrams can be constructed for one set of factorial data with three factors. In each of these 6 cases the line formulas can be found by interchanging in the appropriate way the places of the three factors in the first column of table 2 and by interchanging correspondingly the treatment formulas in the second column. It is evident that every one of the 6 possible diagrams contains the identical amount of information as every other of the 6. According to the author's experience, it seems best to assign the positions to the various factors in order

TABLE 2

Yields of fresh tubers and dry starch in experiment T.503 and corresponding formulas for treatments and regression lines

REGRESSION LINES	FORMAL DERIVATIONS OF FORMULAS FOR REGRESSION LINES	TREATMENT FORMULAS, ARRANGED IN ORDER OF FORMULAS FOR REGRESSION LINES	FRESH-TUBER YIELDS, IN TONS PER HA., ARRANGED IN ORDER OF REGRESSION LINES	DRY-STARCH YIELDS, IN TONS PER HA., ARRANGED IN ORDER OF REGRESSION LINES	COSTS OF FERTILIZING,* IN D.E.I. F PER HA., ARRANGED IN ORDER OF REGRESSION LINES
Potassium line		000–100–200	8.5– 4.0–13.5	2.63– 1.18– 4.16	0– 41– 80
1st, 2nd, 3rd Phosphorus line	(000–010–020) + 000	000–010–020	8.5–11.0– 8.0	2.63– 3.14– 2.19	0– 15– 28
	(000–010–020) + 100	100–110–120	4.0–32.5–40.0	1.18–10.28–12.23	41– 54– 67
	(000–010–020) + 200	200–210–220	13.5–23.0–34.0	4.16– 6.73–10.92	80– 93–106
1st, 2nd, 3rd Nitrogen line	(000–001–002–004) + 000	000–001–002–004	8.5–12.5– 7.0–11.0	2.63– 3.94– 2.23– 3.51	0– 12– 23– 44
	(000–001–002–004) + 010	010–011–012–014	11.0– 5.5– 8.7– 4.0	3.14– 1.45– 2.32– 1.01	15– 25– 36– 58
	(000–001–002–004) + 020	020–021–022–024	8.0–12.5–13.5–11.0	2.19– 3.55– 4.20– 3.47	28– 39– 49– 71
4th, 5th, 6th Nitrogen line	(000–001–002–004) + 100	100–101–102–104	4.0–11.0–11.0–13.5	1.18– 3.46– 3.57– 4.20	41– 51– 62– 84
	(000–001–002–004) + 110	110–111–112–114	32.5–38.0–28.0–40.0	10.28–12.19– 9.45–12.59	54– 65– 75– 97
	(000–001–002–004) + 120	120–121–122–124	40.0–34.5–42.5–53.0	12.23–10.90–13.97–16.91	67– 78– 88–110
7th, 8th, 9th Nitrogen line	(000–001–002–004) + 200	200–201–202–204	13.5–11.0–11.0– 4.5	4.16– 3.20– 3.50– 1.33	80– 90–101–123
	(000–001–002–004) + 210	210–211–212–214	23.0–37.0–23.5–24.5	6.73–10.86– 7.22– 7.29	93–104–114–136
	(000–001–002–004) + 220	220–221–222–224	34.0–38.0–45.0–57.5	10.92–11.13–13.80–17.91	106–117–127–149

* As at time of fertilizing, when \$1 = f 1.82; including costs of application.

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5th Nitrogen line	(000–001–002–004) + 110	110–111–112–114	32.5–38.0–28.0–40.0	10.28–12.19– 9.45–12.59	54– 65– 75– 97
6th Nitrogen line	(000–001–002–004) + 120	120–121–122–124	40.0–34.5–42.5–53.0	12.23–10.90–13.97–16.91	67– 78– 88–110
7th Nitrogen line	(000–001–002–004) + 200	200–201–202–204	13.5–11.0–11.0– 4.5	4.16– 3.20– 3.50– 1.33	80– 90–101–123
8th Nitrogen line	(000–001–002–004) + 210	210–211–212–214	23.0–37.0–23.5–24.5	6.73–10.86– 7.22– 7.29	93–104–114–136
9th Nitrogen line	(000–001–002–004) + 220	220–221–222–224	34.0–38.0–45.0–57.5	10.92–11.13–13.80–17.91	106–117–127–149

* As at time of fertilizing, when $1 = f 1.82; including costs of application.

of descending importance as regards their experimental effect, the primary position being assigned to the factor with the most important effect.

As has been mentioned, in general the choice of the units of abscissas is arbitrary. In diagram 1 the choice has been limited by the practical consideration of obtaining as little intersecting of lines as possible. As has also been explained, in diagram 1 regression is not intercomparable for the different sorts of lines but it is intercomparable within equal sorts of lines. If it is desired to make all the regressions within the whole diagram intercomparable, all the factors should be measured in a single unit and the units of abscissas should be chosen equal for all the factors. Thus, for example, in a water-culture experiment all the food factors might be expressed in terms of osmotic pressure of the factor ions in the culture solution. This may lead to a very important diagram from a physiologic point of view, although much intersecting of lines might thus become a hindrance to the visual effect of the diagram.

In the present field experiment with tapioca, a common unit of abscissas for the three factors is found in the monetary costs of fertilizing. The varying costs per treatment then become the abscissas for the corresponding treatment yields. These costs of fertilizing are to be found in the last column of table 2, and in diagram 2 they have been used as abscissas for the corresponding starch yields, which are to be found in the fifth column of table 2. In diagram 2 the starch yields are measured by their vertical distance from the axis of abscissas, whereas the corresponding costs of fertilizing are measured by their vertical distance from the axis of ordinates.

In diagram 2 a few straight lines have been drawn with the 000 yield-point as the common origin. For every point of such a line the vertical distance from the axis of ordinates measures costs of fertilizing, producing a yield increase of starch, as measured by its perpendicular distance from the 000 point. The quotient of such a cost figure with its corresponding yield figure represents the costs, producing a yield increase of 1 ton of starch. As these quotients are constant within each such line, the points of intersection of such a line with the diagram lines indicate factor combinations for which costs per ton of starch-yield increase are equal to those of all the points of the intersecting line. In diagram 2, such lines, as originating from the 000 point have been drawn for f 5, f 7.50, and f 10 per ton of starch-yield increase. It will readily be seen that diagrams such as diagram 2 may be very important tools in estate practice.

Finally, an example may be given of how factorial diagrams can assist visually in understanding the interrelations between factorial data.

In diagram 1 it is visually clear that a distinction should be made between a low-yield group and a high-yield group, the upper limit for the low-yield group being about 14 tons of tubers per hectare. Furthermore, considering the fact that the treatments have not been replicated, it is equally clear that no statistical significance can be assigned to the differences within the low-yield group. Also it will scarcely need calculation to find a significant difference between the two groups.

It is visually apparent that tuber yield can disengage itself from the low-yield group only if the phosphorus and potassium fertilizer treatments are

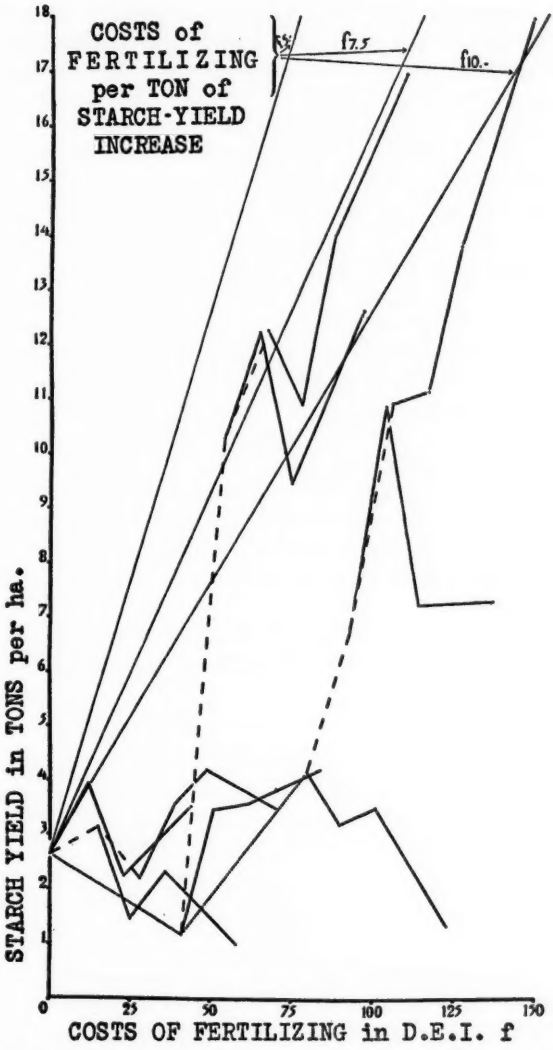

DIAGRAM 2. COSTS OF FERTILIZING AND STARCH YIELDS IN EXPERIMENT T.503

combined. Potassium alone or phosphorus alone, either with or without nitrogen, causes either no or only a statistically insignificant yield increase or

yield depression. It may thus be inferred that either potassium or phosphorus was only just sufficiently available in the soil of experiment T.503 to feed the tapioca for the 000 yield, whereas the other of these two factors, as far as available, could sustain no higher yield or only a statistically nonsignificant higher yield. Nitrogen, however, must have been comparatively much more abundant than either potassium or phosphorus in the soil of the experiment, because without nitrogen large yield increases could be obtained by fertilizing with combinations of potassium and phosphorus.

The 2nd and 3rd phosphorus lines may now be considered as distinct from their dependent nitrogen lines. From the course of the 2nd phosphorus line it is apparent that the single potassium level, combined with the single phosphorus level, gives a large yield increase, and that a further phosphorus addition to such treatment adds little more to the yield effect. The inference from this is that by potassium and phosphorus additions, as in the 120 treatment to the soil of T.503, the ratio of available potassium to available phosphorus in this soil remains or becomes nearly optimal for tapioca-tuber yield. A deduction from this inference is that a potassium addition to the 120 treatment should, by its unbalancing effect on the ratio, depress the 120 yield. Indeed, it is readily seen in diagram 2 that the 220 yield is lower than the 120 yield, the difference being 6 tons per hectare. A further deduction is that the unbalancing effect of the addition of one potassium unit would be larger if the phosphorus level in the treatment were lower. Indeed, diagram 2 shows that the depressing effect of one potassium unit added to the 110 treatment is much larger than that of a similar unit added to the 120 treatment, viz., 9.5 as against 6 tons per hectare.

This may suffice to show the importance of the visual assistance of factorial diagrams in interpreting the interrelations between factorial data.

PHYSICAL CHARACTERISTICS OF SOILS: V. THE CAPILLARY TUBE HYPOTHESIS OF SOIL MOISTURE

AMAR NATH PURI

Irrigation Research Institute, Lahore, India

Received for publication May 12, 1939

The simple concept of the soil as a bundle of capillary tubes to which the laws of surface tension and capillarity could be applied, was one of the earliest attempts to explain soil moisture distribution. What may, therefore, be called the "capillary tube" hypothesis found an early place in the literature. Keen in his review of the subject has rejected the hypothesis (2) mainly on the ground that experimental evidence in support of it has been lacking. The upward capillary movement in soils is effective only to a limited distance, and the theoretical value is by no means approached in actual practice. Even the lowest of these estimates is in excess of the experimental values with tubes of soils, where 4 or 5 feet is seldom reached. The present paper presents experimental evidence in support of the contention that the capillary tube hypothesis is essentially sound and that only defective experimental technic has prevented us so far from realizing in practice the values demanded by theory.

The well-known formula for the height to which water rises in a vertical capillary tube which is wetted by water and the lower end of which is in water is

$$h = \frac{4T}{g\sigma d} \qquad (A)$$

where h = height of meniscus above water level, T = surface tension of water in air, g = acceleration of gravity, σ = density of water, and d = diameter of the capillary tube. Substituting the numerical values (C.G.S. system) in equation (A) we have approximately

$$h = \frac{0.30}{d} \qquad (B)$$

In applying this equation to the rise of water in soil, d must be regarded as the equivalent diameter of a capillary tube made up of the spaces between the particles. The relation between d and the diameter of the particles D has been worked out by Slichter in the case of an ideal soil, i.e., one having particles of the same diameter (9). His analysis shows that the value of d at the widest part of the triangular pores between the particles is 0.288 D where D

is the diameter of the spheres in the ideal soil. Equation (*B*) therefore could be written as:

$$h = \frac{0.30}{0.288D} = \frac{1}{D} \text{ approximately} \qquad (C)$$

In other words, the height of capillary rise is approximately equal to the reciprocal of the diameter of the particles, both quantities being expressed in the same unit.

The capillary theory demands that the soil should be saturated with water at all points between the water table and the upper limit of capillary rise. No serious attempt has been made, however, to ensure this condition in the experiments devised for measuring the upper limit of capillary rise of water in soils. As a matter of fact, any measurement of the capillary force of soil particles obtained by allowing this force to raise water is fundamentally wrong, as it is impossible to dislodge air. Such a procedure is only applicable in a single tube. The futility of such an attempt can be readily realized by trying to fill a sintered glass Büchner funnel completely by forcing water from below. The only logical method of studying the capillary phenomenon in soils is to start from the state of saturation when the capillaries are completely full of water.

EXPERIMENTAL

The apparatus for measuring capillarity, shown in figure 1, is essentially similar to the one used by Haines (1). The ordinary porcelain Büchner funnel used by Haines has been replaced by a sintered glass one, and the pressure deficiency is applied by sliding a burette tube against a graduated scale. The funnel is filled with water by inserting a rubber bung at the top, inverting it, and joining it to the rubber tube leading to the burette. The connecting rubber tube is kept full of water when being joined to the Büchner funnel, and if the burette tap is kept slightly open the flow of water ensures an air-free joint. It is essential that no air be allowed to remain at the lower surface of the filtering disk. Excess of water is removed from the funnel and is replaced by a quantity of sand to give a layer about one-half centimeter thick with some free water standing on top.

At the start, the level of water on top of the sand and in the burette tube is the same. The burette tube is lowered in steps of 1 cm. or so, and the rise of water is noted in terms of the graduations on the tube. This continues until the free water surface over the sand disappears and the capillary pull of the water held in the interstices comes into play. From this point onward, further lowering of the burette tube causes no rise in the level of the water contained in it. This constant value continues until the difference of pressure exceeds the capillary pull of the sand and the water again begins to rise in the burette tube. There is a definite break if the layer of sand is only a few millimeters thick. On the other hand, if the sand layer is a few centimeters thick, the

capillary front recedes as the burette tube is lowered, and some water is yielded at every step. This point will be referred to again.

The water levels in the burette are plotted against the scale readings, and the vertical portion of the curve represents the capillary pull (fig. 2, curve I). When the sand is very coarse and its thickness is over 1 cm., a slight bend is observed in the curve just before the break point (fig. 2, curve II). This is due to the fact that the surface of coarse sand is uneven and some water is held

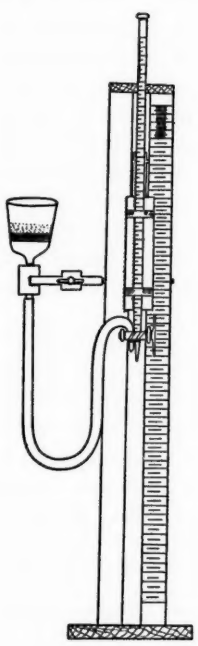

FIG. 1

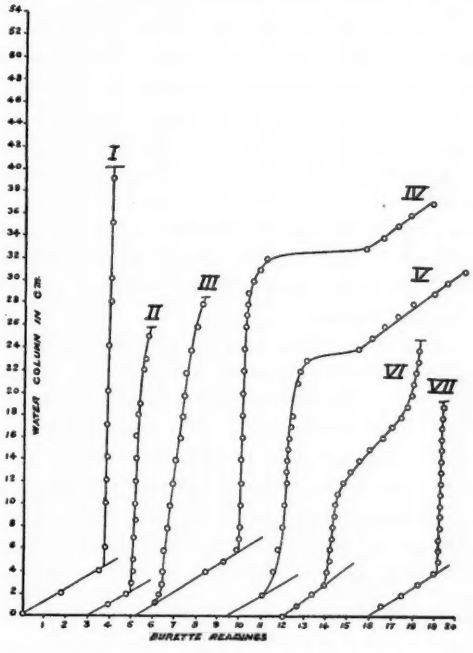

FIG. 2

FIG. 1. APPARATUS FOR MEASURING CAPILLARY FORCE OF AGGREGATES
FIG. 2. DIFFERENT TYPES OF CURVES ILLUSTRATING CAPILLARY FORCE OF AGGREGATES
Ordinate of curve III, Hg column in cm.

in the corner where the sand touches the walls of the Büchner funnel. This water, therefore, is yielded when the capillaries recede in the inside. This corner effect is also pronounced when the sand layer is a few centimeters thick, and the break is followed by another line which is due to the receding capillary front (fig. 2, curves IV and V). It might be pointed out that the introduction of this complication is unnecessary, as a definite break can always be obtained by keeping the layer of sand only a few millimeters thick.

It must be emphasized that there is a limit to the application of pressure deficiency in this particular way, which extends only up to the point that the

capillaries remain *completely* full. The moment the continuity of capillary water is broken and air has entered, the pressure deficiency as applied by lowering the water column has no meaning. Haines failed to recognize this point and carried his pressure deficiency beyond the stage of air entry, i.e., when the capillaries were only partly full. His purpose was to demonstrate the three stages of moisture which he recognized, following Versluys' nomenclature; namely, the *pendular*, the *funicular*, and the *capillary*. It is only in the last stage that the capillaries are supposed to be full and it is only this stage that can be measured with an apparatus of this kind. Any attempt to increase the pressure deficiency beyond this stage can only result in a rupture of the capillaries, and transmission of pressure is rendered impossible. The so-called hysteresis loops obtained by Haines were also due to air spaces which are bound to remain in a moist sand when water is pushed into it from below. It is worthy of note that the filter paper or the sintered glass filtering disk has a capillary pull (fig. 2, curve VII), and if this is greater than that of the sand above, no definite break is observed, in the first instance, because the receding capillaries are again held by the filter paper (fig. 2, curve VI). The capillary pull of the latter, therefore, should always be lower than that of the sand under examination.

With the help of the capillarimeter described, we can measure the maximum capillary force that can develop in a sand or soil and therefore test the relation between the diameter of particles and maximum capillary force. For this purpose, 107 sands and 11 soils were examined. Of the sands, 26 were of uniform diameter and had been separated by the author's siltometer (3) to conform as closely as possible to the diameters given. Others were natural sands obtained from canal beds and were of widely varying origin. The mean diameters of these sands were determined from their distribution curves in the manner described elsewhere (6). These values are compared to the values obtained by the capillarimeter from the relation $h = \frac{1}{D}$ where h is the maximum capillary pull and D is the mean diameter of particles. It will be seen from table 1 A–C that the agreement between the two sets of values is as good as could be expected, and would leave no doubt as to the soundness of the capillary hypothesis, especially as the range of diameters studied is from 0.02 to 4 mm. Alternately the capillarimeter could be used for measuring the mean diameter of sands and soils, and thus is expected to be helpful in studying the regimes of canals which are influenced by the grade of the silt that is passing.

The results with soils need special mention. The clay content of the soils varied from 11.5 to 68.2 per cent, and the mean diameter refers to their distribution curves obtained at maximum dispersion as well as without dispersion. The maximum capillary force actually determined lies somewhere between the calculated values for mean diameter at maximum dispersion and without dispersion (table 1 C). This is what one would expect in view of the uncertainty regarding the state of aggregation of a wet soil. It might be noted that par-

TABLE 1 A

Calculated and found values of capillary columns—natural silts

	MEAN DIAMETER	CAPILLARY COLUMN			MEAN DIAMETER	CAPILLARY COLUMN	
		Determined	Calculated			Determined	Calculated
	mm.	*cm.*	*cm.*		*mm.*	*cm.*	*cm.*
1	.512	19.8	19.5	42	.181	54.7	55.2
2	.501	20.0	20.0	43	.230	35.6	43.5
3	.493	18.9	20.3	44	.205	49.0	48.8
4	.483	19.8	20.7	45	.189	44.0	52.9
5	.476	21.0	21.0	46	.226	43.5	44.2
6	.467	20.6	21.4	47	.126	83.5	79.4
7	.441	23.4	22.7	48	.129	47.4	77.5
8	.432	22.1	23.1	49	.131	78.0	76.3
9	.403	25.5	24.8	50	.136	67.6	73.5
10	.388	26.8	25.8	51	.151	69.0	66.2
11	.389	28.4	25.7	52	.172	57.2	58.1
12	.345	29.6	29.0	53	.178	59.2	56.2
13	.338	31.6	29.6	54	.208	51.6	48.1
14	.325	33.2	30.8	55	.197	61.7	50.8
15	.320	33.0	31.3	56	.202	46.3	49.5
16	.288	41.3	34.7	57	.159	67.4	62.9
17	.255	49.0	39.2	58	.250	41.2	40.0
18	.381	28.0	26.2	59	.133	79.7	75.2
19	.355	26.5	28.2	60	.204	50.6	49.0
20	.278	36.2	36.0	61	.340	29.3	29.4
21	.274	38.0	36.5	62	.363	30.5	27.5
22	.274	36.0	36.5	63	.369	29.3	27.1
23	.330	32.7	30.3	64	.313	32.2	31.9
24	.353	32.0	28.3	65	.242	44.7	41.3
25	.711	17.5	14.1	66	.205	45.0	48.8
26	.646	21.4	15.5	67	.306	35.7	32.7
27	.636	17.8	15.7	68	.225	42.1	44.4
28	.624	17.6	16.0	69	.227	43.7	44.1
29	.231	44.4	43.3	70	.269	34.0	37.2
30	.332	31.3	30.1	71	.356	27.2	28.1
31	.227	41.4	44.1	72	.215	48.0	46.5
32	.141	66.4	70.9	73	.201	43.5	49.8
33	.117	94.3	85.5	74	.261	40.5	38.3
34	.166	56.9	60.2	75	.245	37.7	40.8
35	.185	55.5	54.1	76	.250	40.8	40.0
36	.188	55.3	53.2	77	.283	35.0	35.3
37	.201	52.5	49.8	78	.351	28.8	28.5
38	.216	46.4	46.3	79	.263	39.0	38.0
39	.179	64.3	55.9	80	.338	28.8	29.6
40	.223	47.1	44.8	81	.332	24.7	30.1
41	.147	42.7	68.0				

ticles having diameters of 0.02 cm. or more settle quickly to the bottom of the funnel, and the remaining soil behaves as if it were devoid of these particles. In calculating the mean diameters of the soils, the portion of the distribution

curve above 0.02 cm. diameter is not taken into consideration, and the results are calculated as if these particles were absent. Another point worthy of note is that soils should be soaked in water for 24 hours before their capillarity is measured. A layer of fine sand is spread on the sintered funnel with some free water at the top. Dry soil is gradually added on top of the sand layer and allowed to soak in the water for 24 hours. After this the capillary force is

TABLE 1 B

Calculated and found values of capillary columns—silt and sand fractions

	MEAN DIAMETER	CAPILLARY COLUMN	
		Determined	Calculated
	mm.	*cm.*	*cm.*
1	3.0 –4.0	3.5	2.9
2	2.0 –3.0	5.4	4.0
3	1.3 –2.0	6.3	6.1
4	1.0 –1.3	8.8	8.7
5	0.88 –1.0	13.0	10.6
6	0.6	14.4	16.7
7	.56 – .60	23.2	17.24
8	.49 – .56	24.4	19.0
9	.44 – .49	27.4	21.5
10	.40 – .44	26.6	23.8
11	.36 – .40	29.7	26.3
12	.34 – .36	30.6	28.6
13	.31 – .34	32.8	30.8
14	.29 – .31	36.3	33.3
15	.28 – .29	36.3	35.1
16	.26 – .28	37.8	37.0
17	.25 – .26	36.7	39.2
18	.22 – .25	41.1	42.6
19	.20 – .22	44.9	47.6
20	.19 – .20	46.0	51.3
21	.17 – .19	50.4	55.6
22	.15 – .17	55.9	62.5
23	.13 – .15	69.1	71.4
24	.12 – .13	77.0	80.0
25	.08 – .12	90.6	100.0
26	.065– .08	94.1	137.9
Lead shots			
1	1.32 –1.5	6.8	7.1
2	1.0 –1.32	7.9	8.6

measured as usual. The part of the curve after the capillarity comes into operation and the free water surface has disappeared, is not vertical (fig. 2, curve III). Unlike sands, soils yield some water at every increase of pressure deficiency. There is also a corresponding decrease in the volume of the soil as the water is squeezed out and the particles come closer and closer. This phenomenon is entirely due to the swelling of soil colloids and is not funda-

mentally related to the moisture content and pressure deficiency. Increasing deviations from the vertical simply indicate increasing amounts of colloids. The point will be referred to again. As equilibrium is also reached at a much slower rate in soils than in sands, at least 15 minutes are allowed between successive readings. While studying the capillary force of soils, it is not convenient to work with water columns 3 or 4 m. long. The burette tube and a part of the connecting tube is filled with mercury, therefore, and the pressure deficiency is applied by lowering the mercury column, which can be converted into terms of the height of water column, if required. In table 1 C, the calculated and found values of capillary pull of soils are given in terms of the mercury column.

TABLE 1 C

Calculated and found values of capillary columns—soils

SOIL NUMBER	CLAY (.002 MM.)	MEAN DIAMETER*		CAPILLARY COLUMN†		
		Dispersed	Undispersed	Determined	Calculated	
					Dispersed	Undispersed
	per cent	*mm.*	*mm.*	*cm.*	*cm.*	*cm.*
P.C. 1	11.50	.0246	.0373	22.80	30.00	19.79
2	64.06	.0229	.0730	18.8	32.23	10.11
3	68.21	.0233	.0737	21.3	31.67	10.01
4	15.56	.0329	.0499	24.4	22.43	14.79
5	12.79	.0342	.0475	18.5	21.58	18.54
6	29.73	.0326	.0642	19.0	22.64	11.50
8	27.30	.0497	.0789	17.4	14.85	9.35
9	22.90	.0493	.0863	9.0	14.97	8.55
10	38.62	.0394	.0845	21.0	18.73	8.73
11	35.08	.0435	.0980	16.0	16.97	7.53

* Excluding particles over 0.2 mm.

† Height of mercury.

It has already been pointed out that if the sand column is long, there is no break, but a sharp bend through the vertical part of the capillary curve corresponds to the maximum capillary pull. An important question arises in this connection as to what might be the moisture gradient in a sand column with the receding capillary front. It is also important to know whether the moisture content of the sand column above the capillary front is influenced by the extent to which the latter has been lowered. In other words can the receding capillary front draw down some moisture from the top or has the sand column above the capillary front no connection with it, so that it could be removed without affecting the state of equilibrium of the lower part. A column of sand 100 cm. long was made by filling with sand glass tubes 2.2 cm. in diameter and 10 cm. long, joined with rubber tubing, taking care that all the air was displaced and there was free water at the surface. The tube was then allowed to drain, by gradually lowering the water reservoir.

After 24 hours, during which the top of the tube was protected from evaporation, the glass sections were separated by slitting the rubber joints vertically and making a clean cut by running a wire across the sand column. The various sections were immediately transferred to lead moisture tubes (7), and moisture content was determined by evaporating to dryness at 100–110°C. The results are plotted in figure 3. It will be seen that there is an abrupt change in the moisture content. The smoothness of the curve drawn through the midpoints is only indicative of the fact that the receding capillary front is not a sharp line. Actually the difference between its lowest and its highest points may be 5 or 6 cm. An absolutely sharp rise cannot be expected in view of the fact that the sections were chosen at regular intervals from the top and not from the capillary front, which was almost in the middle of one of the sections.

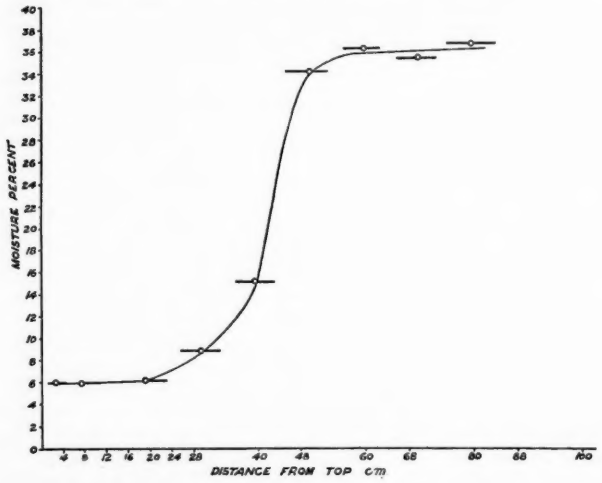

FIG. 3. MOISTURE DISTRIBUTION IN A SAND COLUMN UNDER A RECEDING CAPILLARY FRONT

The results leave no doubt, however, that in the capillary phenomenon, the capillaries are either full or empty. It is important to note that there is no connection between the top part at 6 per cent moisture and the lower part at 35 per cent moisture except through stray capillary tubes of short length just above the receding capillary front. The removal of the upper glass sections had no influence on the lower ones, which remained at the same moisture content, and the connecting burette tube showed no change in reading.

In order to determine whether the residual moisture content of the sand, when the capillaries have emptied, is characteristic of the particle size, a number of sands were examined in a similar way by applying pressure deficiency until the capillary front had receded far down. The results, plotted in figure 4, show that there is a correlation between the size of the particles (D) in milli-

meters and the residual moisture percentage (M). This relation may be expressed by the formula:

$$M = \frac{1.65}{D}$$

No special significance seems to attach to the value 1.65 in this formula, beyond the fact that the moisture content would reach a very high value when the diameter of the particles was less than 0.1 mm. In soils with an average diameter of the order of 0.02 mm. the corresponding moisture contents would assume ridiculously high values. The limited applicability of the formula therefore should be recognized. It appears, however, that as the particle size becomes smaller, the difference between the moisture content when the capillaries are full and the residual moisture, narrows and in extreme cases might become negligible.

Schofield has endeavored to express the moisture content of soils in terms of free energy relationship (8). If we suppose that water is held by soil against

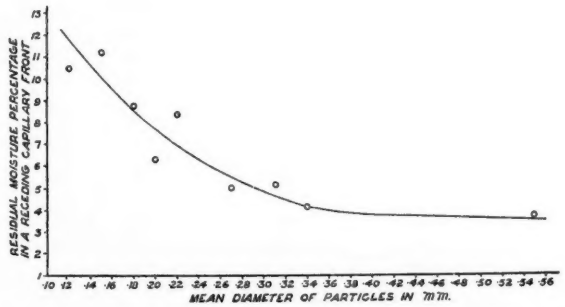

FIG. 4. RELATION BETWEEN PARTICLE SIZE AND RESIDUAL MOISTURE IN A RECEDING CAPILLARY FRONT

a suction force tending to displace it, the free energy can be expressed in terms of the height in centimeters of the equivalent water column. In order to deal conveniently with the whole range of suction, use is made of the logarithm of this height. By analogy with Sørensen's logarithmic acidity scale, the symbol pF has been used (F being the recognized symbol for free energy). From equation (C) we can express the relation between the diameter D of particles and its pF as:

$$\text{pF} = -\log D \qquad (D)$$

We can, therefore, express the summation curves of soils in terms of free energy, or pF. Such curves, of course, will not be different from the ordinary summation curves on the semilogarithmic scale, but they will bring out more clearly the fact that in soils we have particles of a diameter which can form capillaries

of the order demanded by theory. Summation values and other relevant data for two soils are given in table 2. Particles up to the diameters corresponding to pF 5.03 were determined by the pipette method; values for pF 6 are extrapolated from the summation curves. It is admitted that not much reliance can be placed in the extrapolated values on a logarithmic scale, but there is no mistaking the general trend of the extrapolated portion. These soils are of unusual interest, because in spite of the fact that P.C. 123 contains a much higher percentage of conventional clay than does P.C. 13, the former absorbs less moisture at all humidities below 93 per cent, as will be seen from figure 5. At this humidity, corresponding to pF 5, the curves cross,

TABLE 2

Relation between diameter of particles and their summation percentages for two soils

DIAMETER	pF	SUMMATION PERCENTAGES		RELATIVE HUMIDITY
		P.C. 13	P.C. 123	
cm.				*per cent*
.006	2.22	93.4	98.0	.....
.004	2.40	89.5	98.1	.....
.002	2.70	88.0	97.9	.....
.001	3.00	79.0	97.0	.....
.0008	3.10	77.0	96.8	.....
.0005	3.30	73.0	96.0	.....
.0002	3.70	58.8	90.9	.....
.0001	4.00	56.9	87.9	99.5*
.000043	4.37	48.6	74.7	97.0
.000023	4.64	46.2	59.0	96.5
.000016	4.80	45.0	49.8	95
.0000094	5.03	45.7	39.2	92
.000001	6.00	40.0	12.0	40
.0000001	7.00	....	....	0

* Calculated from the formula:

$$pF = 6.5 + \log_{10}(2 - \log_{10} h)$$

where h is relative humidity.

and at higher humidities P.C. 123 absorbs more moisture than does P.C. 13. It will be seen that pF 7, which corresponds to the oven-dry state, also marks the lower limit of the colloidal state (particles of diameter 10^{-7} cm.). It is interesting to note that particles of diameter 10^{-7} cm., corresponding to pF 7, will have a capillary diameter of the order of 3×10^{-8}. The diameter of water molecules is of the order of 3.45×10^{-8}. In other words, the particles of this size will be packed so closely that even a single molecule of water could not be squeezed into the interspace. Such colloidal particles can render a soil completely impervious to water. The sodium carbonate method of lining canals and water courses for preventing seepage losses, devised by the writer (4), is based on this principle. It aims at converting a Ca-soil into a

Na-soil; the latter being highly dispersed fills the interstices with colloidal particles, leaving very little space for the water to pass through. It is significant how the colloidal state in soils merges into the molecular state. It is therefore not difficult to understand that many of the so-called adsorption phenomena in soils may be essentially of a chemical nature and in no way different from similar reactions in molecular dispersions, i.e., solutions.

The extreme limit of conventional clay, i.e., particles of 0.0001 cm. diameter, corresponds to pF 4, which is equivalent to a relative humidity of 99.5 per cent. Particles of larger diameters therefore give capillaries that are too coarse to be filled through the vapor phase. This explains the often quoted fallacy that it is not possible to saturate a soil completely from a fully saturated atmosphere. It is also clear that the region of hygroscopicity lies below the

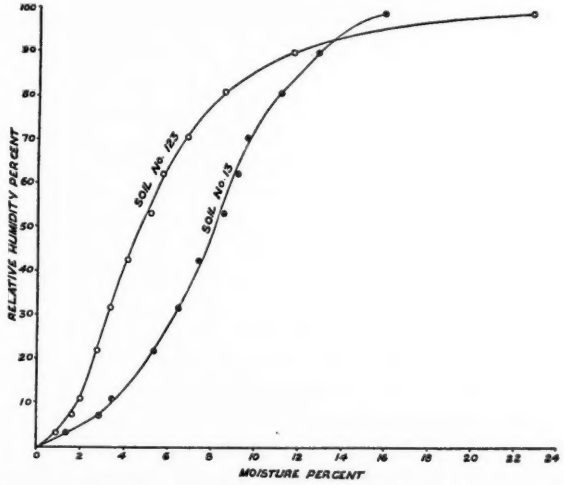

FIG. 5. RELATION BETWEEN MOISTURE CONTENT AND RELATIVE HUMIDITY IN TWO SOILS

conventional clay, and an explanation of the varying hygroscopicity of clays lies in the size distribution of the ultraclay particles. A semiquantitative relation between conventional clay and hygroscopicity is also apparent from these considerations. A general similarity in the shape of the mechanical analysis summation curves and relative humidity moisture content curves can also be understood. This similarity would be still more striking if we could compare the ultramechanical analysis of particles smaller than the conventional clay.

We have seen that a sand consisting of particles of 0.01 cm. diameter requires a suction pressure of the order of pF 2 to overcome the surface tension of the water held in the capillaries. We can therefore vary the pF from 0 to 2 without altering the moisture content. For a finer sand, say 0.001 cm.

diameter, the suction force must exceed pF 3 before any water can be drawn out. It is clear, therefore, that there must be an abrupt drop in the pF-moisture content curve. In soils, this abrupt drop is masked by secondary effects, and as the pressure deficiency is increased, some water is yielded at every step. We shall therefore endeavor to visualize the cause of this apparent anomaly. The phenomenon of swelling of soil on absorbing water is well known, but its mechanism is not quite clear. We are generally content with the statement that water somehow can make room for itself by separating the particles a little from one another. The real situation can be very well imagined if we recall the property of "auto-disintegration," by virtue of which soil colloids go into suspension without being shaken (5). We can imagine the larger interstices between compound particles as being just filled with water. This is followed by the auto-disintegration of colloidal clay, which is accompanied by an increase in volume, because the particles that were originally most closely packed are no longer so. In the end the capillaries are filled not with water but with a highly viscous fluid constituting a clay suspension of great density. In the extreme case the bigger particles can float in this suspension, and the entire mass becomes plastic. If suction is applied at this stage, water filters out and the volume decreases correspondingly. This continues until the soil aggregates are most closely packed. That this might be a true picture of the swelling of soils is supported by the fact that this phenomenon is most pronounced in Na- and Li-soils, the colloidal clays of which are known to impart to the soil the property of auto-disintegration. The yield of water from a saturated soil by suction, therefore, is due to the filtration of water from the clay suspension held in the interstices, and the force required is used in overcoming the elastic rigidity of a thick suspension. The relation between pF and moisture content in this region is, therefore, not real and is due to the capillaries being full not with water but with a clay suspension. The absorption and removal of water from a soil is a slow process, and the attainment of equilibrium may take several days. An interesting experiment may be cited to illustrate this phenomenon. If to a saturated sand column held under a pressure deficiency some water is added, the whole of that water passes on to the burette tube of the capillarimeter. If the soil is held in a large Büchner funnel and water is added drop by drop, the only visible effect is a rise of water in the burette tube exactly equal to the volume of water added. On the other hand, if the experiment is repeated with soil, the water may take several days to pass on to the burette tube, and even then some of it may be retained in the soil. This part goes to swell the soil mass. Similarly, soil may continue to yield water for several days under a certain pressure deficiency. It is for this reason that determination of a true volume for the capillary pull of soils is difficult. Even the approximate values leave no doubt, however, that the forces involved are the same both in sands and in soils.

It must be emphasized that the process of emptying the capillaries is dis-

continuous. A certain critical pressure deficiency is required to overcome the surface tension. The relative humidity-moisture content curves show no discontinuity because there is no discontinuity in the size distribution. The equilibrium moisture at every vapor pressure merely indicates that the capillaries formed by particles up to a certain limiting size are full, and the capillaries in the larger sizes are empty. When the vapor pressure is lowered, another set of capillaries corresponding to a lower size are emptied.

This view gives a new orientation to our concept of the wilting coefficient of soils. The fact that the wilting coefficient of soils is of the order of pF 4.2 (5) is likely to give an erroneous idea of the mechanism of moisture absorption by root hairs. For instance, it would seem that the limiting factor was the suction pressure of the soil, and a possible connection between the suction pressure of roots and that of the soil might be sought. A moment's reflection will show that this view is likely to be misleading. The limiting factor in the utilization of soil moisture may be not the suction pressure but the limiting size of the root hairs which cannot penetrate capillaries below a certain diameter. The development of the suction pressure in soils is entirely due to the surface tension, and unless a root hair can enter and establish contact with the water surface, the plant cannot take up the moisture. This condition of isolation begins to operate when the moisture has receded to the capillaries formed by particles of 0.0001 cm. diameter corresponding to pF 4. The importance of clay fraction in determining wilting coefficient is at once apparent. Since clay represents only the upper limit of particles of this size, however, the exact relation must depend on the size distribution of finer particles in the clay fraction. Particles coarser than clay are mainly responsible for retaining moisture that is available to plants; clay merely helps in the conservation of this moisture. It might be pointed out that in working out the relation between the capillary pull and the mean diameter of soil particles, the lowest limit of size for calculating the mean diameter was taken as 0.0002 cm., in spite of the fact that there were finer particles which would have reduced the mean diameter considerably. The main contention that emerges from these considerations is that there is a limit to the continuity of the liquid phase when pressure deficiency or suction force is applied to soils. When this force exceeds that required to empty capillaries formed by particles coarser than clay, gaps are created through which transmission of pressure deficiency can not take place. If a wet soil is placed on a dry soil, the suction applied by the latter cannot be transmitted when the soil has been dried to pF 3.3 (field moisture). Although centrifugal force is not limited by similar considerations and it is theoretically possible to reduce the moisture content to any value down to dryness, there are practical difficulties in the production of such an enormous force and we are again limited to a pF value of 3 (moisture equivalent). Plants, on the other hand, through their minute root hairs can reach much smaller capillaries, but it must be emphasized that the limiting factor is not the suction pressure of roots but the size of the capillaries. It is for

this reason that the wilting coefficient must be regarded as a soil characteristic which bears no relation to the suction force of the roots. In fact, it is doubtful whether the so-called suction force of roots plays any part in the intake of water from soils.

In considering the rise and distribution of water in a dry soil through capillarity, a fundamental mistake is made in laying too much emphasis on the vertical height from the free water surface. The whole idea of Buckingham's capillary potential is based on the erroneous assumption that the height of the capillary front is the limiting factor. As a matter of fact, the capillary movement is uninfluenced by gravity and is the same in all directions. In order to visualize the mechanism of the rise of moisture in a dry soil, we must remember that this movement can take place only from larger to smaller capillaries. In other words, a dry soil will only withdraw moisture from a wet soil if the former contains some capillaries smaller than the largest ones in the latter which may be full of water. Each layer of dry soil therefore draws water from the wet layer next to it, and the mean diameter of particles responsible for this pull becomes smaller and smaller as the distance from the free water increases, until the capillaries required for exerting the pull are so small that they are unable to establish contact and the visible movement stops. We have thus a sharp line dividing the wet and the dry soil. The total height of the capillary moisture attained in this way bears no relation to the suction force of the soil except qualitatively. It is, however, related to the size distribution of particles which determine the size of the capillaries. The moisture gradient is governed by the height of the capillary column only incidentally. The free energy due to height has no meaning in this case, and any section of the tube could be cut off and turned upside down without altering the moisture distribution. The lowest moisture content at the highest point is not due to the fact that water is being held against a greater height, but because the thinnest capillaries could not be used to draw out water from the section next to it. The abrupt stoppage of moisture movement is not due to the fact that the capillary force is unable to support a higher water column, but because still smaller capillaries are unable to withdraw water on account of their inability to establish physical contact with the water surface in the larger capillaries. When we speak of the abrupt stoppage of moisture movement, we refer only to the wetness visible as a change in the color of the soil. It must not be inferred, however, that there is no movement of moisture beyond this point. Actually there is, but it is confined to capillaries which are too small to show their wetness. As a matter of fact, this movement is very important in connection with the movement of salts in soils. It can be shown that salts move with water even when the moisture content of the soil corresponds to a relative humidity of 75 per cent or pF 5.6. This movement can be stopped, however, by interposing a layer of sand, the capillaries of which may be too large to draw out water from the finer capillaries in the soil. This principle has been successfully used in preventing salt efflorescence on earth roads in salt areas.

Since the height of a column of liquid supported by capillaries of a given diameter varies directly as the surface tension of the liquid and inversely as the capillary diameter, this relation could be used for comparing surface tensions of liquids other than water. For instance, if Tl is the surface tension of a liquid and Tw the surface tension of water, then:

$$Tl = Tw \cdot \frac{Hl}{Hw} \qquad (E)$$

where Hl and Hw are the heights of the capillary columns for the liquid and water respectively. Since Tw is constant and Hw can be kept constant by using particles of the same diameter, (E) can be written:

$$Tl = KHl \qquad (F)$$

TABLE 3

Surface tension and interfacial tension values of liquids determined by the capillarimeter, compared with standard values

LIQUID	SURFACE TENSION		INTERFACIAL TENSION	
	Found	Standard	Found	Standard
Benzene	34.9	28.9	37.8	35.0
Phenetole	32.5	32.7	33.0	29.4
Amylbutyrate	29.4	25.2	18.3	23.0
Hexane	21.8	18.4	48.8	51.1
Ethyl ether	18.3	17.1	10.3	10.7
Toluene	....	....	38.1	36.1
Oleic acid	....	....	18.3	15.6
Xylene	....	....	41.4	37.8
Iso-butylchloride	....	....	24.2	24.4
Mesitylene	....	....	33.0	38.7
p-Cyanine	....	....	31.2	34.6

in which K is a constant characteristic of the grade of sand used. The surface tension values of a number of organic liquids were determined by means of (F), sand of 0.475 mm. mean diameter being used. The results, given in table 3, show a good agreement with the standard values from the International Critical Tables. The experiments were extended to the determination of interfacial tensions between water and some organic liquids lighter than water. These liquids were floated on the water. When the free water surface disappeared as a result of the application of pressure deficiency, the interfacial tension came into play. The break point was as definite as that in the water-air interface. Actually no sand was used in this case. The porous plate of the sintered glass funnel was used for applying the capillary tension. The value of K in equation (F) was 7.335 in the case of interfacial tensions. No particular significance, however, can be attached to this value, which is worked out from the straight line relationship between the capillary height and inter-

facial tension. A comparison of the interfacial tensions determined in this way and standard values, also given in table 3, shows a good agreement. The liquids chosen were those available in the laboratory, and no special care was taken to ensure their purity, as the whole object of the experiment was to illustrate a principle rather than elaborate a method of measuring surface tensions. There is no doubt, however, that the method is capable of refinement and might be employed, with some modification, for measuring surface tensions.

SUMMARY

Evidence is brought forth in support of the capillary tube hypothesis of soil moisture. Determination of capillary force of soils by measuring the maximum height to which moisture can rise, is fundamentally wrong. This can be done only by completely saturing the soil and applying gradually increasing suction pressure until the capillaries break. This force is correlated with the size of particles as demanded by theory.

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Thomas D. Rice
1878–1939

In the death of T. D. Rice, soil science has suffered the loss of one of its active workers. Mr. Rice passed away suddenly at his office on August 23.

He was born at Arredondo, Florida, on April 16, 1878. His boyhood days, for the most part, were spent on the farm of relatives in Randolph County, North Carolina. In 1900 he received the degree of bachelor of philosophy from the University of North Carolina. His major interest was mineralogy, and during his senior year in the university he was an assistant instructor in geology under Collier Cobb.

Shortly after graduation, Mr. Rice accepted a position with the Division of Soils, U. S. Department of Agriculture, at which he stayed until his sudden and untimely death.

During the earlier period of his work in the department, Mr. Rice was in charge of various field parties making soil surveys and special soil investigations in different regions of the country. In 1914 he explored, with H. H. Bennett, the soil conditions in Alaska. In the same year he was promoted to inspectorship and assigned to the West Central States. From that time Mr. Rice, in close association with Dr. Curtis F. Marbut, divided his time between inspection trips throughout the Middle West and the tireless review of numerous soil survey reports.

Only those who were close to him during his life know what a surprisingly large volume of work was done by Mr. Rice during the 25 years of his inspectorship. Several hundred reports passed through his hands. To every page and every line of them he gave his careful attention. All the field data for these reports were examined by him and thoroughly discussed with the field men during the inspection trips. He did his work with amazing patience, never losing his temper and never claiming any credit for himself. The credit was given to the field party; his was only a modest mention in the list of names—"T. D. Rice, Inspector, District 3."

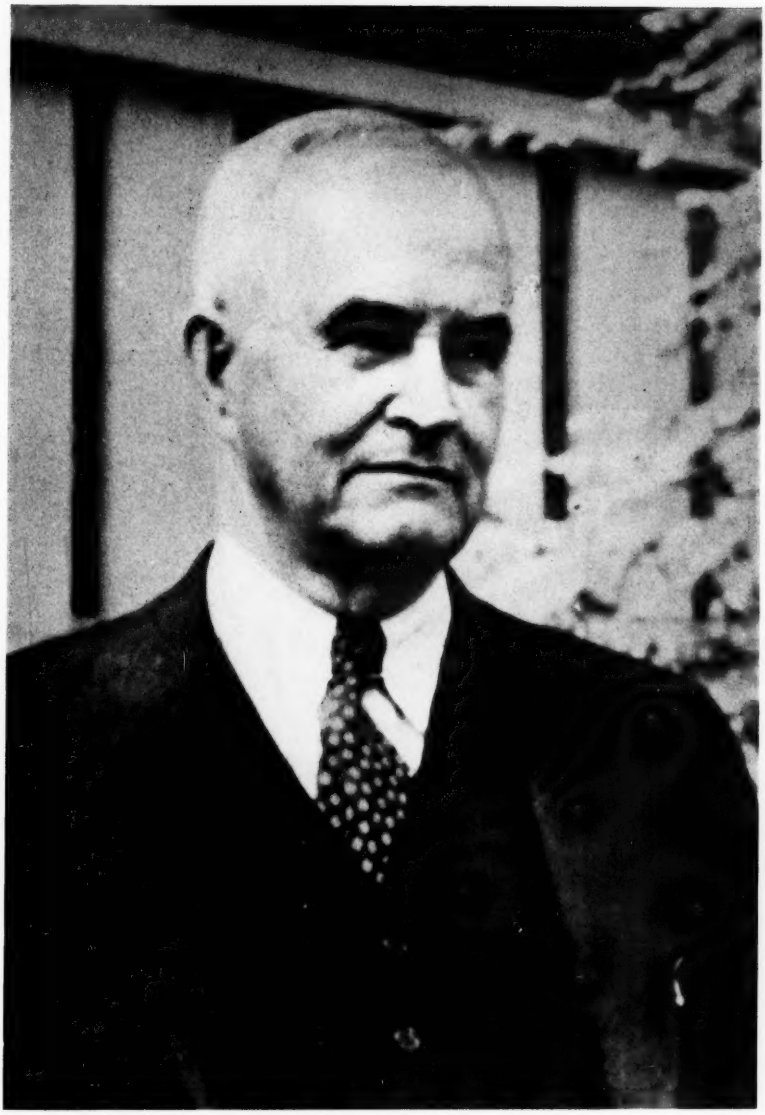
Unassuming, entirely free from selfish ambition, Mr. Rice did not leave many individual contributions to soil science. He generously gave most of his life to the less spectacular but not less important task of helping others to do their parts in exploration, survey, and description of the soils of the United States. In this way he faithfully served soil science for almost 40 years.

He entered the field of soil investigation in the United States almost at the beginning of this work and was one of the few pioneers in the field. This group headed by Milton Whitney began their work at the time when soil science was just emerging from its infancy. They organized the investigation,

worked out the method and technic of survey, and developed a system of correlation and classification of soils which gradually became known throughout the world as the American system. At the same time, they had to train the young cadre of field men and to lead and supervise the field work throughout the country. The work progressed rapidly in close cooperation with various state organizations, and from it grew the American School of Soil Science.

Mr. Rice devoted most of his life to the building up of this school. As a charter member of the American Soil Survey Association, which grew into the Soil Science Society of America, he had a particular, almost parental interest in that organization. He did not miss a single meeting and gave much of his time and energy to its development. Sometime a historian of this period of development of soil science undoubtedly will mention many men who contributed to its progress. He will mention Whitney, Marbut, Lyon, Emerson, Shaw, and others. Mr. Rice's name may not appear in the list. This, however, will by no means obscure or diminish the value of his contribution to the collective work.

Modest and rather shy in his life, genuinely unassuming in his work, Mr. Rice persistently avoided being in the front row of the various organizations and societies of which he was a member. In spite of his rare experience and thorough knowledge of soils, he was eager to learn rather than to appear in the rôle of a teacher. A friendly, somewhat timid smile, a complete lack of ostentation, and a kindly humor were his unfailing characteristics.



THOMAS D. RICE

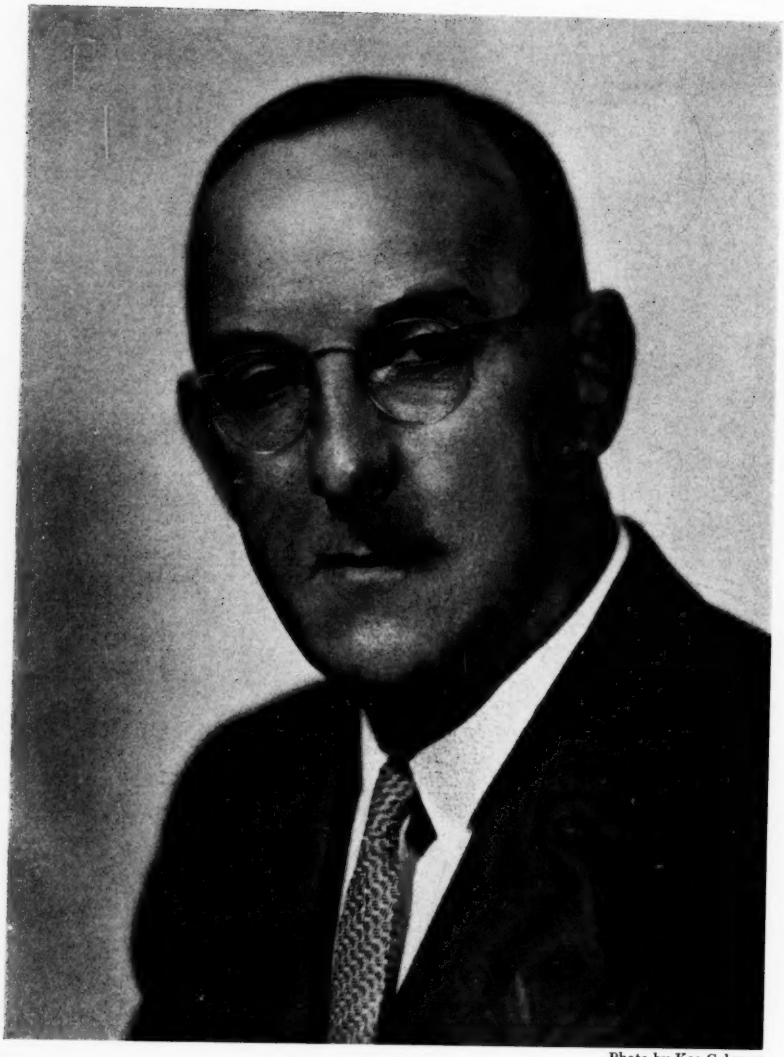


Photo by Kee Coleman

CHARLES FREDERICK SHAW

Charles Frederick Shaw
1881–1939

Charles F. Shaw, professor of soil technology in the University of California, died at Berkeley, California, on September 12, after a brief illness.

Professor Shaw was born in West Henrietta, New York, May 2, 1881, and was graduated from Cornell University in 1906. That year he served as scientific assistant in the Bureau of Soils, U. S. Department of Agriculture. The following year he joined the staff of the Pennsylvania State College as instructor, and two years later was promoted to the assistant professorship of agronomy. In 1913 he was called to the University of California to a position which he occupied and faithfully filled, except for brief periods of leave, until his death.

Professor Shaw actively prosecuted soil surveys in California throughout his 26 years in the state, and probably no other person had such a complete knowledge of its soils. In addition to carrying on his soil survey work, he headed the division of soil technology and taught soils courses to hundreds of students in the University of California. Professor Shaw took great interest in his students and in student activities and was very popular both with his students and with his colleagues. As leader of the soil surveys and of the division of soil technology, he was pre-eminently successful.

Professor Shaw was widely traveled. He visited and studied soil and agricultural conditions in Australia, New Zealand, Hawaii, and many other regions and countries. In 1930 he was visiting professor of soils at the University of Nanking where he conducted extensive field studies in China and laid the basis for systematic soil surveys later undertaken. The summers of 1926 and 1928 were spent in Mexico in an advisory capacity to the national commissioner of irrigation in teaching and training a corps of men in soil surveying. He served at various times on advisory committees and in field investigations for the U. S. Reclamation Service and other federal and state organizations.

He was a member of the International Society of Soil Science and official delegate of the University of California to the congresses of this society held in Washington, Russia, and England, in the proceedings of which he took active part. He was also an active member of the American Soil Survey Association throughout the period of its existence and played a prominent part in bringing about the consolidation of this association with the Soils Section of the American Society of Agronomy, resulting in the formation of the Soil Science Society of America. He was a Fellow of the American Society of Agronomy, of the American Geographical Society, and of the American

Association for the Advancement of Science, and a member of the American Society of Agricultural Engineers, the Western Society of Soil Science, California Academy of Sciences, Alpha Zeta, and Sigma Xi.

His publications and work are well known, and his influence with students was exceptionally fine. His thoroughness and enthusiasm for soil work were outstanding, and his sympathetic cooperative spirit endeared him to all his colleagues and friends. His loss is keenly felt in California.

W. P. KELLEY

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